Q 583
P 8
XXII-XXIV

ANNEX
LIBRARY
B
055751

Cornell University Library
BOUGHT WITH THE INCOME
FROM THE
SAGE ENDOWMENT FUND
THE GIFT OF
Henry W. Sage
1891

A.273256 11/IV/13
9724

Cornell University Library
TP 5.I6 1912
v. 2
Eighth International congress of applied
3 1924 015 343 449
olin, anx

Cornell University Library

The original of this book is in
the Cornell University Library.

There are no known copyright restrictions in
the United States on the use of the text.

http://www.archive.org/details/cu31924015343449

ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS OF APPLIED CHEMISTRY

Washington and New York

September 4 to 13, 1912

SECTION Xb
PHYSICAL CHEMISTRY

VOL. XXII

ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS OF APPLIED CHEMISTRY

Washington and New York
September 4 to 13, 1912

SECTION Xb
PHYSICAL CHEMISTRY

VOL. XXII

E.V.

8383
P4
~~XXII~~-XXIV

A.273256

The matter contained in this volume is printed in exact accordance with the manuscript submitted, as provided for in the rules governing papers and publications.

La matière de ce volume a été imprimée strictement d'accord avec le manuscrit fourni et les règles gouvernant tous les documents et publications.

Die in diesem Heft enthaltenen Beiträge sind genau in Übereinstimmung mit den uns unterbreiteten Manuskripten gedruckt, in Gemässheit der für Beiträge und Verlagsartikel geltenden Bestimmungen.

La materia di questo volume e stampata in accordo al manoscritto presentato ed in base alle regole que governano i documenti e le publicazioni.

THE RUMFORD PRESS
CONCORD·N·H·U·S·A·

ORIGINAL COMMUNICATIONS

TO THE

EIGHTH INTERNATIONAL CONGRESS

OF

APPLIED CHEMISTRY

APPROVED

BY THE

COMMITTEE ON PAPERS AND PUBLICATIONS

IRVING W. FAY, CHAIRMAN

T. LYNTON BRIGGS	JOHN C. OLSEN
F. W. FRERICHS	JOSEPH W. RICHARDS
A. C. LANGMUIR	E. F. ROEBER

A. F. SEEKER

SECTION X*b*.—PHYSICAL CHEMISTRY

Executive Committee

President: W. R. Whitney, Ph.D.
Vice-President: Alexander Smith, Ph.D.
Secretary: Arthur B. Lamb, Ph.D.
A. A. Noyes, Ph.D., Sc.D., LL.D.
G. A. Hulett, Ph.D.

Sectional Committee

Jerome Alexander, M.Sc.
Frederick J. Alway, Ph.D.
S. Lawrence Bigelow, Ph.D.
B. B. Boltwood, Ph.D.
W. C. Bray, Ph.D.
John W. Brown, Ph.D.
Geo. K. Burgess, D.Sc.
H. P. Cady, Ph.D.
F. G. Cottrell, Ph.D.
Wm. L. Dudley, B.S., M.D.
H. W. Foote, Ph.D.
Francis C. Frary, Ph.D.
C. McCheyne Gordon, Ph.D.
W. E. Henderson, Ph.D.
John Johnston, D.Sc.
H. C. Jones, Ph.D.
Louis Kahlenberg, Ph.D.
G. N. Lewis, Ph.D.
Herbert N. McCoy, Ph.D.
R. B. Moore, B.S.
Theodore W. Richards, Sc.D. Ph.D., LL.D.
M. A. Rosanoff, Sc.D.
Julius Stieglitz, Ph.D., Sc.D.
James H. Walton, Ph.D.
E. W. Washburn, Ph.D.
S. W. Young, B.S.

And the Sectional Executive Committee

VOLUME 22

SECTION X*b*.—PHYSICAL CHEMISTRY

CONTENTS

Bancroft, Wilder D., and Briggs, T. R.
Blue Gelatine-Copper 7

Benedicks, Carl.
Allotropy of Iron and Silveriodide 13

Beutner, Reinhard.
Die physikalische Natur bioelektrischer Potentialdifferenzen 29

Boving, Henrik. See Menzies, Alan W. C.

Briggs, T. R. See Bancroft, Wilder D.

Burgess, George K., Sc.D.
The Present Status of the Temperature Scale 53

Colson, M. Albert.
Sur les Theories et les formules de la Chimie-Physique 65

Coombs, Leslie Briggs. See Forbes, George Shannon.

Forbes, George Shannon, and Coombs, Leslie Briggs.
A New Method of Measuring the Pressure of Corrosive Gases at Constant Volume 79

Frankforter, George B., and Frary, Francis C.
Equilibria in Systems containing Alcohols, Salts and Water, Including a new Method of Alcohol Analysis 87

Frary, Francis C. See Frankforter, George B.

Garver, M. M.
On the Polymerization of Liquids and a General Method for Determining its Relative Value 129

Hildebrand, Joel H.
The Relation Between the Potential of Liquid Amalgam Cells and the Constitution of the Amalgam 139

Hildebrand, Joel H.
The Vapor Pressure of Zinc Amalgams 147

Ikeda, Kikunae.
Contributions to the Chemical Kinetics of Enzymes 157

Jonker, W. P. A.
Abstract of the Paper on Caoutchouk-Benzene (C_6H_6) — *Water* 169

Kanolt, C. W.
The Melting Points of Fire Bricks 171

KUNZ, JAKOB.
On the Present Theory of Magnetism and the Periodic System of Chemical Elements 187

LICHTY, D. M.
Some Physical Constants of Sulphur Trioxide.—Melting and Boiling Points, Density, Coefficient of Expansion and Molecular Weight 205

MAHIN, EDWARD G.
The Constitution of Aluminates 207

MARIE, CHARLES.
Tables Annuelles de Constantes et Donnes Numeriques de Chimie de Physique et de Technologie 209

MENZIES, ALAN W. C., and BOVING, HENRIK.
The Vapor Pressures of Some Concent ated Zinc Chloride Solutions 219

REYCHLER, PROF. DR. A.
Contributions à l'étude des savons 221

RINDELL, ARTHUR.
Solubility in cases of altered solid phase 233

UYEDA, KENJIRO.
On Mixed Crystals of Potassium and Ammonia Chlorides 235

VAN DORP, DR. G. C. A.
Equilibrium in the system of sulphuric acid, sulphate of ammonia and sulphate of lithium. at .30° C 239

VAN DORP, DR. G. C. A.
On the determination of the worth of tanning material, specially for tanning fishing nets 241

WIEBE, PROF. DR.
Die Prüfung von Laboratoriumthermometern 245

WOUDSTRE, H. W.
The System Oxalic Acid Oxalate of Ammonia and Water at 30° and 45° 251

YAMASAKI, EIICHI.
Abstract of the Studies on the Chemical Kinetics of Catalase 259

ZSIGMONDY, RICHARD.
Zur Systematik der Kolloide 263

BLUE GELATINE-COPPER

By Wilder D. Bancroft and T. R. Briggs
Cornell University, Ithaca, N. Y.

Copper and the copper alloys such as brass and the bronzes lend themselves very readily to artistic decoration by means of colored superficial films or "patinas." Great as is the variety of colors which may thus be imparted to copper, nevertheless a rich and true blue patina for this metal is practically unknown. It was while seeking such a blue surface film that the electrolysis of copper acetate solutions containing gelatine was first performed. One gram of gelatine was dissolved in 325 ccs. of a 1% solution of cupric acetate and this mixture electrolyzed between carefully cleaned and burnished electrodes of sheet-copper. The electrolysis was continued for five minutes at a cathode, (and anode) current density which varied between 0.15 and 0.45 amp dm_2. The process was carried out at room temperature.

The electrolysis performed, the cathode was found to be covered on its inner surface with a thin, pale brown deposit, which, when rubbed with the fingers was seen to possess a peculiar, slippery surface caused by a very appreciable amount of gelatine deposited simultaneously with the metallic copper. No gas became visible at either pole during the passage of the current.

In itself, this pale brown cathode deposit gave no indication of its peculiar properties and it was by chance only that these were discovered. An electrode, freshly coated with a layer of the gelatine-copper was by an oversight allowed to remain in the solution of copper acetate from which the film of metal had just been deposited and the current was turned off. On removing the electrode from the solution, it was noticed that the brown color originally possessed by the cathode film had given place to a purplish blue of extraordinary brilliance and beauty. This led to further experiments.

A second electrode was then coated with a film of gelatine-copper and, after careful rinsing with cold tap water, immersed in a 5% solution of copper acetate containing no gelatine. Straightway there ensued a remarkable series of color changes upon the surface of the copper deposit; hues of startling evenness and intensity followed each other in regular succession until the electrodes had acquired a magnificent deep-blue coloration. This process we shall speak of as a "development," since it bears a certain resemblance to the development of the silver image in the process of photography.

EXPERIMENTAL

1. *Effect of Gelatine*

After the process of development had been discovered, a more systematic study of the formation and nature of gelatine-copper was undertaken. It then became evident that gelatine must be present in the electrolyte and that this colloid exerted a tremendous influence upon the nature of the cathode deposit. The term "gelatine-copper" was thus justified. The optimum gelatine concentration was found to lie between 0.25 and 0.66 per cent. The electrolysis of copper acetate solutions containing no gelatine failed to give the developable films nor was it possible to substitute other hydrophile colloids such as starch or gum-arabic for gelatine or glue.

2. *Nature of the Electrolyte*

Electrolysis of copper formate, acetate and propionate solutions containing gelatine resulted in cathode films which developed blue in copper acetate although this development was imperfect in the case of the deposits from the formate solution. Copper sulphate solutions of different strengths and varying gelatine content failed absolutely to give developable deposits. Similar results were obtained with solutions of copper nitrate and chloride.

3. *Effect of Temperature*

Variation of the temperature at which the electrolysis was performed led to interesting results. Between 20° and 40° C., the cathode deposit was of the usual pale brown color and gave a more or less satisfactory color-development to blue in copper acetate. At 50° C. or at higher temperatures, the cathode deposit was colored a bright red or a brick red and was unaffected by the developing solution. Between 55° and 60° a short electrolysis with a low current density gave a gold-colored but very thin film which had a rather iridescent appearance. These gold and red films can be lacquered with complete success and are interesting in their application to metallochromy.

4. *Other Factors*

The best results were obtained with copper acetate or propionate solutions made up in the proportion of 1 or 2 parts by weight of the crystallized salt to 100 parts of water. The electrolyte should be neutral or at most but very slightly acid. The current density must be low—between 0.15 and 0.45 amp dm_2—and the process need not exceed 5 minutes in duration. The nature of the metal used as cathode is of little importance as long as the copper solution is not decomposed. Thus with nickel, brass, and platinum, good deposits were obtained as adherent cathode films which developed a good blue color.

5. *The Development of the Blue Color*

A 5% copper acetate solution containing no gelatine was used as the developing bath throughout this work, although a copper propionate solution may also be employed. Copper formate developer gave less satisfactory results. A large number of other salt solutions were then tried as developers with practicably no success. Thus in normal copper sulphate solution a film of gelatine-copper was colored a dull, dark indigo. In N/50 copper sulphate a fairly good blue color was developed although the colors obtained with sulphate solutions are distinctly inferior to those prepared with acetate developer. Very dilute copper nitrate oxidized the film to dark brown copper oxide while a chloride solution spoiled the deposit entirely.

Several oxidizing solutions were next used with negative results. Potassium chromate, bichromate, permanganate, perchlorate, chlorate, and persulphate failed to give even a trace of blue coloration. The films were usually oxidized slowly to brown cupric oxide. Reducing solutions gave no development. The film of gelatine-copper was unaffected by dilute, warm, hydrazine hydrate and underwent accelerated blue development in copper acetate after such treatment.

A solution of sodium acetate gave no blue coloration of the copper film nor was it otherwise with the acetate solutions of other metals. Hence this phenomenon must be a function of the copper contained in the developing solutions.

6. *Reverse Development*

An electrode, covered with a deep blue film, was immersed in a very dilute aqueous solution of hydrazine hydrate and, in a short time, bubbles of nitrogen began to form on the blue surafce. The blue color then slowly faded away, until, passing in the reverse direction through the series of colors previously described, the film of gelatine-copper again took on its original brown color. This process was called a "reverse development."

The reverse development completed, the electrode was rinsed in distilled water and once more immersed in the usual copper acetate developer. The blue color formed again quickly, but was a bit thin and uneven.

If a film of gelatine-copper is allowed to stand undeveloped for several hours, it completely loses its power of developing in copper acetate. This is probably due to its oxidation by the air because it was found that treatment of such a "dead" film with hydrazine hydrate was sufficient to regenerate its powers of development. The same result was obtained with a film after immersion in warm, dilute hydrogen peroxide—no development occurred until the layer of oxide so produced had been reduced with hydrazine.

THEORY AND CONCLUSIONS

Schützenberger, by the electrolysis of copper acetate solutions, obtained at the cathode a peculiar form of copper; and, being unable to explain its unusual behavior, he announced it as an allotropic modification. Wiedemann incorrectly contended that the new form of copper was really the oxide of that metal, while recently Benedicks has advanced the idea that we have to deal with a solid solution of acetic acid in copper. It can be shown, however, by a careful study of their results and by consideration of the facts of colloid chemistry, that the allotropic copper of Schützenberger is merely the normal metal in the form of an irreversible colloid gel.

The same conclusion is applicable to the deposits of gelatine-copper described in this paper. The gelatine acts here as the "protecting colloid," migrates by cataphoresis to the cathode, and there inhibits the growth or crystallization of the copper nuclei. Gelatine-copper is an irreversible gel of colloidal copper. The whole phenomenon is but another example of the marked influence of organic and other colloidal substances upon metals prepared by electrolysis, accounts of which have appeared in the recent papers of Müller and Bahntje, Snowdon, and others.

What is the nature and mechanism of the process of the color development? This is indeed a difficult problem, chiefly because of the exceeding small quantities of reacting material of necessity dealt with. The blue, although a superficial color, is nevertheless not the color of a thin film of gelatine or oxide bringing about interference disturbances in the reflected rays of light. Nor does it seem to be the color of a definite chemical compound. The blue layer does contain oxide as is shown by its action in hydrazine and yet it cannot be prepared by any process of simple oxidation. It cannot be produced by the partial coagulation of the copper gel.

It was shown by Wiedemann that Schützenberger's copper possesses the power of adsorbing very considerable quantities of copper oxide from copper acetate solutions. This observation furnished the clue to the process of development. The color changes that appear upon the film are the result of *a surface adsorption of hydrous copper oxide from the copper solution.* The hydrous copper oxide is present as a suspension in very appreciable quantities in the acetate or propionate solutions, being the product of hydrolytic dissociation. This being the case, we should expect the best development with the acetate solutions and but little color effect with the sulphate and chloride developers.

The reversal of development caused by hydrazine is due to the reduction of the adsorbed oxide. There seems to be a certain definite concentration of oxide in the copper film necessary for the production of a blue color. As the concentration of the oxide increases by continued adsorption, the film passes through the series of colors so distinctive of the development.

In conclusion it can be said in support of this hypothesis that it is in accord with many of the established facts in colloid chemistry and explains in the best possible manner this decidedly obscure phenomenon. Stannic oxide adsorbs gold from suspension and forms the "Purple of Cassius"; under very special conditions colloidal copper adsorbs hydrous copper oxide and similarily gives an intensely colored adsorption compound.

SUMMARY

The electrolytic production of a form of colloidal copper was performed with certain copper solutions containing gelatine.

This new form of copper develops a remarkable series of colors when immersed in certain copper solutions, a peacock-blue being the finest color obtained.

The process of development is an adsorption of hydrous copper oxide by the surface of the colloid film.

There have been described methods of coloring metal objects gold, golden-brown or red.

ALLOTROPY OF IRON AND SILVERIODIDE

By Carl Benedicks
Stockholm, Va. Sweden

For the metallography of the iron, its allotropy is still the most vital question. Although it seems as though a certain, even if indistinct, agreement has been attained regarding the existence of α, β and τ—iron, there still remains considerable work to be done, even for chemistry in general. It is therefore best that we, first of all, clearly indicate what we mean by allotropy and what different cases are to be taken as possible; after that account for some special determinations on silveriodide, and finally discuss the influence these may have on the opinion about the allotropy of iron.

I. DEFINITION OF ALLOTROPY

Theoretical transformation curves

The properties of a body, whether simple or compound, usually change with the temperature of the body. But sometimes the dependence on the temperature is especially perceptible. At a certain temperature (or at a definite number of temperature points) a sudden transformation of the properties of the body takes place, a change of modification, which according to the customary terminology (Berzelius, 1841) is called allotropy if the body is simple (a chemical element), but polymorphy if it is compound (chemical combination). These definitions are, however, not strictly adhered to (compare J. Meyer, list of literature); in the following, with W. Ostwald, we use the word allotropy for both cases.

We will now try to more precisely express the conditions which may be comprised as allotropy. We only take into consideration ordinary equilibrium (*i.e.*, we presume that the properties of the body are at any temperature and under all conditions independent of time).

Now suppose that we have determined a certain property's quantitative dependence on the temperature. If the curve thus obtained show a point of discontinuity—that is, if at a certain temperature an infinitely small temperature change causes a finite change of the property, we say that the temperature is an allotropic point of transformation for the body in question (strictly: in regard to the property chosen) and the temperature of transition is said to be the limit between two allotropical modifications of the body.

The property which is usually put in the first place is the relation to absorption of heat, its sudden transition usually brings about easily seen changes in the speed of cooling or heating. As a rule such a point of transition is noticed in several properties, but need not be perceptible in all. (The definition given has the same range as it already had with Berzelius, and which J. Meyer still considers the most suitable, *i.e.*, it embraces also those modifications which take place at the transition between the different so-called states of aggregation.)

The chosen property can in the proximity of the point of change be thought to depend on the temperature in four principally different ways:

I. The change from *b* to *c* Fig. 1, I, occurs at the transition temperature T quite suddenly, so that in neither the curve *a-b* for the α-modification nor *c-d* for the β-modification can any deviation be observed from the course "normal" at some distance from T.

The transformation α/β occurs perfectly sharp. There can be no hesitancy here: the transformation takes place sharply at the temperature T. The body alters properties abruptly; there is no continuous transition α/β, which may also be so expressed that the two modifications are insoluble in each other.

This is the ideal case which usually presents itself to the mind as an expression for an allotropical transformation.

II. It may be thought that *one* of the curves *ab* or *cd* diverges more or less from its "normal" course (shown by dots in Fig. 1) when the temperature approaches to T, thereby getting nearer the other curve (Fig. 1, II:a and II:b). The transition α/β is less sharp; we may express this saying that the β-modification has a *limited solubility* in the α-modification, or *vice versa*.

III. It is further possible that both *ab* and *cd* in the proximity

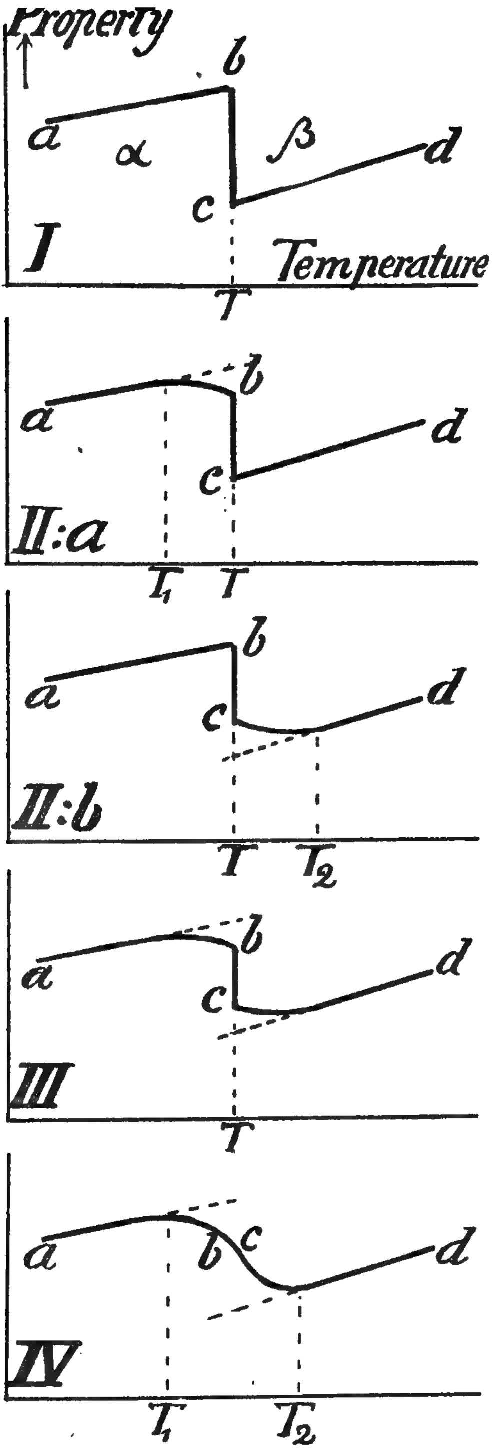

Property
b
a
α
β
d
c
I
Temperature
T
b
a
d
c
II:a
T_1
T
b
a
d
c
II:b
T
T_2
b
a
d
c
III
T
c
a
b
d
IV
T_1
T_2

FIGURE 1

of T diverge from the respective normal course (Fig. 1, III). Hereby the transition α/β becomes still less sharp. In analogy with the foregoing one may say that *both modifications have a limited solubility for each other.*

IV. It cannot be left out of account that the transition between both the normal curves *ab* and *cd* occurs in a *perfectly continuous manner* (Fig. 1, IV). In this case, which may also be said to mean unlimited solubility between the supposed modifications, no allotropic transformation *point* will, in the sense of the definition, be found; but it may be fully justified to speak of a *transformation range* T_1 T_2. Illustrations of this case are to be found in liquid state (for ex. sulphur), and in gases with molecules dissociating at increasing temperature (as gas of iodine); compare also page 26.

We have thus to take into consideration cases I–IV. In the physical chemistry the conviction is gradually working its way in, that *one always has to take into account a certain solubility between two bodies.* Solubility between two modifications of the same body and solubility between two different bodies can not be said to present any principal difference.

One may therefore dare to assert that the most presumptuousless supposition regarding an allotropic transformation is that its course is that of type III, which embraces the others as special cases; afterwards one ought in every case give attention to the experimental determinations of how large the deviations from the normal lines (*ab*, resp. *cd*) may be; or, in other words, to what degree a reciprocal solubility may be supposed.

From the foregoing theoretical transformation curves those obtained by *experimental determinations* will always deviate more or less; it is probably taking great consideration to the faulty sources possible (especially temperature differences), which has been the cause that only case I has nearly always been supposed.

A sure illustration of case I may probably be had in the transformation points at 83° C. and 35° C. for nitrate of ammonium (for which the calculated coefficient of pressure, according to Tammann and Luossana agrees with the observed, see Roozeboom).

A transformation curve of type II:b has been long known, namely for the substance H_2O, where one has been obliged to suppose that the modification ice is to a certain degree soluble on the modification water, whereby the remarkable minimum of volume at 4° C. is explained.

In the following we will find illustrations of case II:a.

II. THE ALLOTROPY OF SILVERIODIDE

The experiments for verifying for silveriodide the well-known Thomson formula for the pressure coefficient for the transformation temperature have, as is known, been unsuccessful.

Tammann found a value that was about 4 times too great, and Mallard and Le Chatelier a still larger value for the pressure coefficient, dT/dp.[1]

Thus: Tammann presumes still another (a third) AgJ-modification, occurring somewhere below the transformation temperature 147° and supposes that the hexagonal modification (stable below 147°) can solve (a certain amount of) the regular (stable above 147°); Roozeboom finds the occurring of the third modification unclear and demands better proofs for the supposed solubility.

As Maxwell in his Theory of Heat, p. 8, has pointed out, silveriodide is acknowledged as the only known body which contracts at increasing room-temperature. I have a long time considered this singular fact as a proof that at increase of the temperature from the room-temperature in the hexagonal modification there arises a small quantity of the regular modification, which according to Rodwell has a considerably lower specific volume (an intense contraction occurring when the temperature rises to 147°).

If this interpretation is correct, one will — as the regular modification may be thought solved in the other only in the proximity of the point of transformation — come to the conclusion that at temperatures lying *considerably below* that of the room-temperature the silveriodide may have a positive, normal coefficient of expansion.

The following *Determinations of the Dilatation of Silveriodide from* −180° *to* +200°, were carried out.

---

[1] See Roozeboom's *Die heterogenen Gleichgewichte* I, 130.—I quote Roozeboom in extenso about this: "Tammann (Wied, Anm. 68, 646) hat nun bewiesen, dass dies einer anderen Verwandlung des hexagonalen AgJ zugeschrieben werden muss, *die etwa unterhalb* 100° *auftritt, deren Verhältnisse aber nicht gut aufgeklärt sind.* Er vermutet dass die Abweichung der von 145° ausgehende Kurve vom berechneten Wert durch die Annahme erklärt werden könnte, dass *das hexagonale AgJ mit dem regulären Mischkrystalle bilde.* Bevor eine derartige Annahme zulässig ist, sind jedenfalls deutlichere Beweise erwünscht."

For this purpose a small apparatus of fused silica was constructed, which permitted a mirror-reading of the dilatations (even of as small test-staves as 10 x 1 mm.).

The dilatation apparatus was surrounded by a double-walled cylinder, containing a heating spiral so that the whole could, after having been put into liquid air, easily, by means of a suitable current, be adjusted at any temperatures whatever between that of liquid air and room-temperature.

The temperature was measured with a thermo-element, the junction of which was in close proximity to the test-stave. The test-staves were made by sucking molten silveriodide into thin-walled glass-tubes which had been sooted on the inside (being spontaneously blown off at the cooling at the temperature of

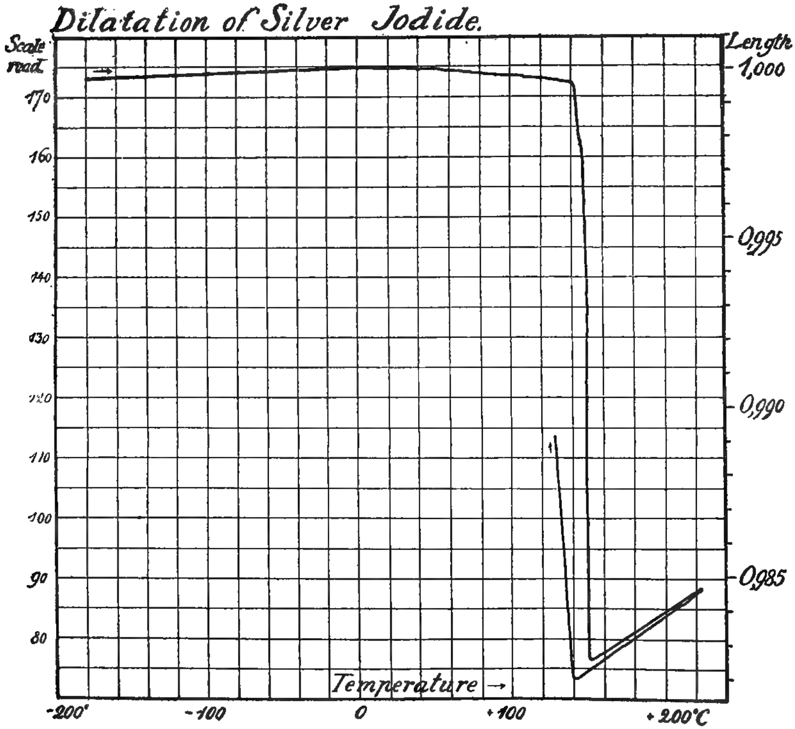


FIGURE 2

transition. Of the two series between −180° C. and +206° C., which agree very well, the one is graphically illustrated in Fig. 2.

From this we infer *that at low temperatures*, at which no earlier measurements have been published, *the silveriodide resembles almost all the other known bodies*, *i.e.*, that it has a normal, positive coefficient of dilatation.

At increasing temperatures this grows less and becomes 0 in the proximity of 0°. After that a weak contraction gradually takes place, slowly increasing to +140°, when a very sudden contraction occurs, during which the temperature was taken to 149°.[1] After the transformation the mass has a considerably larger coefficient of dilatation. This latter aspect of the curve corresponds very well to that obtained when using the figures published by Rodwell.

The transition of the silveriodide at about 147° thus corresponds to the type II: a.

If the determinations of electrical conductivity, propounded by Kohlrausch are represented graphically (by using a logarithmic scale), you get the impression that these determinations also indicate that the transition progresses continuously from lower temperature to that of the point of transition.

What has now been quoted may therefore be considered to prove that at least one transformation of type II: a is known. Through this Tammann's supposition as to the solubility between the hexagonal and the regular modifications is also confirmed. On the other hand, there seems scarcely to be any reason for accepting the supposition of a third modification, as the properties of that may probably be explained through the solubility just mentioned; in other words: if you persist on a third intermediary modification, the simplest hypothesis will, however, be that it only consists of hexagonal silveriodide, which in solution contains a certain limited amount of regular silveriodide.

III. THE ALLOTROPY OF IRON

Historical

When turning our attention to the iron, we will call to mind the following words of one of the most fundamental investigators in this branch. F. Osmond[1] says: "il est regrettable que les traités modernes négligent l'histoire et présentent commes des monuments achevés des sciences en perpetuelle évolution".

---

[1] According to Monkemeyer the point of transition is 146.7°

The history in this case does not go far back.

Without knowledge of the earlier works of Gore (1869), Barrett (1873), Tait (1873), F. Osmond and J. Werth deposited on July 9, 1883, at the Academy of Sciences at Paris, a sealed manuscript containing all the principal conclusions which later on were given in the work "Théorie cellulaire des propriétés de l'acier" which was published by them in 1885.

Specially through calorimetric measurements showing 5.2 to 15.0% greater content of energy in quenched steel than in annealed the existence of two different allotropic modifications of the iron were considered as surely proved. "α dominating in annealed steel, β mixed with α in quenched steel in varying amount according to hardness." Different physical properties, such as malleability, density, supported the conclusion that allotropy is present.

In the following important work of Osmond: "Transformation du fer et du carbone" (1887), it is for the first time stated that α-iron is soft, β-iron in itself hard and brittle. From cooling-curves taken by means of Le Chatelier's thermo-element (1887) there was, then, evidenced: (1) sudden transformation of Ar_3" at about 890°; (2) a more undecided retardation of the cooling, "Ar_2", at 750–700°. An *r* inserted means cooling, a *c* heating, Osmond opined that only the transformation A_3 occurs suddenly as ordinary allotropic transitions at a definite temperature and that A_2, on the contrary, is, though without distinct boundaries, spread over a long interval of temperature. It was therefore supposed that there exist only two allotropic conditions, α and β, but that the transition from the one to the other may be either discontinuous or progressive. In a new work of 1890 Osmond (III) further discusses the nature of Ar_2 and finds it probable that this transformation is simply "the end of Ar_3, retarded by the presence of a little carbon". Between Ar_2 and Ar_3 the metal is a mixture of the two varieties α and β. There is nothing mentioned about a third modification. The cautious reservation with which Osmond hitherto has mentioned Ar_2—the "Achilles-heel" of the theory of allotropy—seemed all the more justified when Roberts-Austen, in the first of the celebrated "Reports to the Alloys Research Committee," 1891, on a photographically registered temperature-time curve, taken on carefully electrolytically purified iron (accurate analysis by E. Riley showed 0.007% C.), found a distinct standstill corresponding to A_3 but no traces of A_2; on a material given by Osmond (with 0.16% C.) Ar_2 appeared, however, even with this less sensible method.

---

[1] *Ferrum, poème latin* . . traduit en vers français par F. Osmond, Paris, 1906, p. 57.

The existence of A_2 was given an unexpected support in a work by Arnold (1894), who considered that he had proved that A_2 surely exists quite independent of A_3, which Osmond had not dared to state up to that time. Even somewhat earlier (1892) Osmond (V) had himself found that the loss in magnetism corresponds to A_2 and not, as he originally supposed, to A_3. Le Chatelier opined (1894) that A_2 and A_3 must be considered clearly differentiated on account of the magnetic behaviour. The magnetic determinations were considered to have received a good support in P. Curie's renowned work on the magnetism of bodies (1895), and when Osmond (VI) published his classical work on the constituents of steel he came to the logical conclusion of the individual existence of A_2: α-iron below A_2, β-iron between A_2 and A_3, and γ-iron above A_3.

Osmond (VII) was, however, not satisfied with regard to A_2, which he discusses in a paper of 1899, with the conclusion: that several facts seem to indicate that the point Ar_2 extends in reality to a much lower temperature than, say, 700°.

A similar opinion against a decisive transformation was also uttered by Howe and the unsuccessful attempt made by Le Chatelier (1899) to find some discontinuity in dilatation-curves corresponding to A_2, may have given rise to doubts regarding the real existence of A_2.

From the crystallographic investigations made by Osmond (VIII, IX) (in conjunction with Cartaud) it was found that the crystalline forms of α and β iron are identical, while that of γ-iron differs.

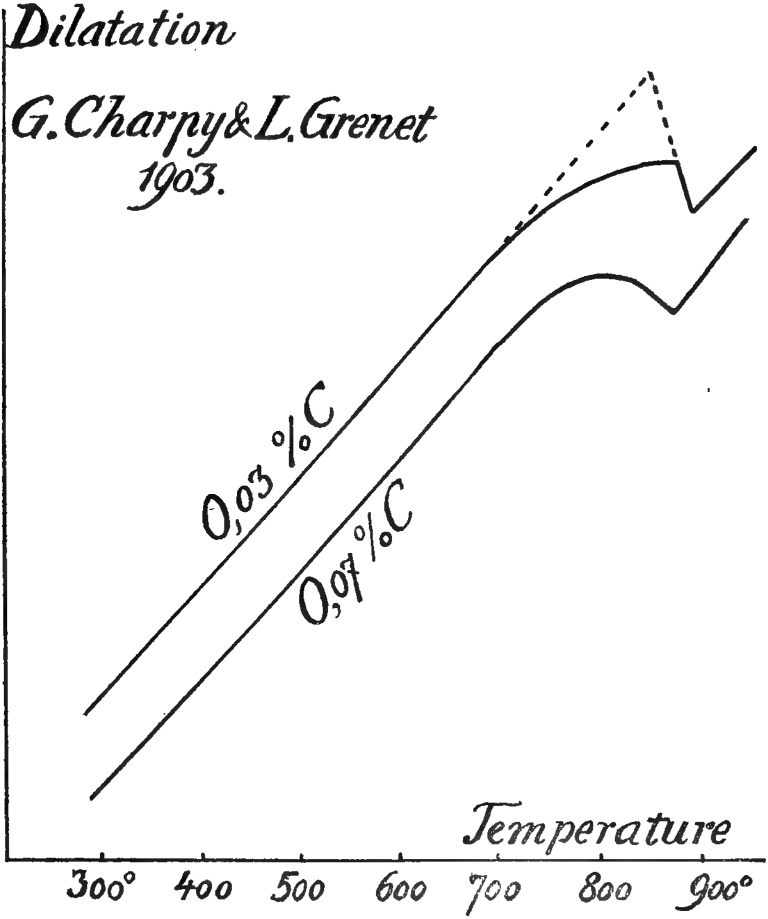


FIGURE 3

Hadfield also declared (1910): "It is doubtful whether any definite facts are available that β-iron exists at all."

In a very clever work of Rosenhain and Humfrey, to which we will later come back, some facts came forth which seemed to be a very strong support for the conclusive existence of A_2 and that the hardness of the iron does suddenly increase within the β-region.

The Present Situation

That A_3 corresponds to an actual transformation point is evident. The question is if A_2 also does so. The most important points favouring this view we will now critically review.

1. The existing cooling-curves show such large divergencies (not mentioned in the preceding), that the thermical determinations cannot be brought forth as proof that A_2 is a transformation point in the sense defined above.

2. After a closer inspection of Curie's determinations using really appropriate graphics (logarithmic scale, as given already by Curie himself) it is evident that an *important* part of the decrease of susceptibility has occurred at a temperature corresponding to A_2 (about 770°) but *by no means to all of it:* the decidedly most prominent magnetical transformation lies, as Osmond first thought, at about 900° or coincides with A_3. The correctness of this is evident from the last work by Weiss and Foëx.

3. If the investigations of Rosenhain and Humfrey be closely analyzed one will, it is true, find that the iron in the β-interval is harder than that within the adjoining α-region, but they cannot serve as a proof that there is any sudden transformation between α and β iron.

From the above it is evident that there is no reason left to prove a discontinuity at A_2. On the contrary, there is an excellent reason for full continuity, namely, the dilatation determinations of Charpy and Grenet, illustrated in Fig. 3, showing that Ac_3 at 890° corresponds to quite a sharp contraction, Ar_2; on the contrary, as I stated in 1904, to a decided though fully continuous digression from the "normal" (dotted) curve.

Our investigations thus give the following results:

The iron shows a perfectly clear transformation point at about 890°, Ar_3; this is distinctly bounded against higher temperatures, but not against lower ones. *The transformation of the iron at 890° thus belongs to the type II: a* which has been shown possible and the actual existence of which has, in the foregoing, been proved for silveriodide.

In accordance therewith A_2 is to be taken in connection with the temperature interval below 890°, within which (on cooling) the dilatation, magnetic properties, etc., have not yet taken the course which is the normal one for the lower temperatures.

By using the nomenclature of Osmond it may be stated thus:

Above the allotropic transition point 890° there is the γ-iron, which does not seem to be able to dissolve any modification existing at lower temperatures.

The modification α-iron, which is stable at lower temperatures, has a certain solubility for the γ-modification which increases with the temperature; at about 750° this solubility is so large that the properties of the iron are *perceptively* influenced by it.

The iron, β-iron, which according to the definition exists between 770° and 890° is to be considered only as *α-iron which in solid solution contains a certain, limited quantity of γ-iron.*

This is in analogy with the presumed third AgJ-modification which is simplest explained as hexagonal AgJ, which in solid solution contains a certain, though limited, quantity of regular AgJ, increasing with the temperature.

It is not difficult to explain that the β-iron nevertheless has quite specific properties, especially hardness; this must depend on the state of solid solution, thereat supposing that another modification acts as foreign matter.

It is thus evident that what is called β-iron possesses some different properties (especially in regard to hardness) from the α-iron. But the question whether the α-iron and the β-iron are different allotropic modifications ought probably to be answered negatively; the question is reduced to this: whether the α-modification in the region T_1 T, Fig. 1, II:a, is to be counted as an allotropic modification, different from the α which exists below T_1.

The opinion expressed here about the β-iron is of a certain interest in connection with the ferronite-hypothesis expounded by the Author in 1904, which from this point of view gains in plausibility and may be said to embrace that at a lower content of carbon (below 0.5% carbon) the ferrite consists of pure α-iron, but at higher percents of carbon, the ferrite consists of α-iron with a certain quantity of dissolved γ-iron, causing a certain solubility of carbon (0.27%). During the last year, the said hypothesis seems to have gotten a valuable experimental confirmation through the calorimetric investigations (cooling-curves) by Arnold.

As regards the widely varying heat-developments which have been noted during cooling, at Ar_2, the explanation of such will probably have to be looked for, as Osmond originally supposed, in the presence of a certain quantity of carbon or other foreign matter retarding the transformation of A_3. A specially significant hint to this is that no development of heat was observed at the investigation (Roberts-Austen) using the purest iron made, analyzed, and up to date.

SUMMARY

1. The very common opinion that *allotropy* means a quite sudden transformation from the one modification to the other can not, *a priori*, be maintained except as a special case (Type I, Fig. 1). There is always the possibility that the one modification (Type II: a and b) or both (Type III) have a certain solubility for the other — this is the simplest expression for the fact that the transformation *partly* takes place continuously. If the solubility were unlimited one could not speak of allotropic transformation point, but allotropic modifications can nevertheless be said to occur. (Type IV.) Which of the types of allotropy (theoretically) possible, that actually occur in each case, must be decided by experimental study of one, preferably more, of the properties in the proximity of and at a sufficient distance from the transition point in question.

2. An experimental study of the dilatation of silveriodide, extended to −180°, has shown that the transformation point of this body at about +147° is an illustration of type II: a. At low temperatures the silveriodide has a *positive* dilatation (Fig. 3, p. 22); only at 0° or room-temperature the well-known *negative* dilatation occurs, that is peculiar to silveriodide. The dilatation must be ascribed to a solubility increasing with the temperature in the hexagonal modification of the regular modification stable above the transition point, a solubility which, according to the curve of dilatation, is in all probability greatly limited.

The supposition of a certain solubility has earlier been made by Tammann, but for want of clear proofs rejected by Roozeboom; determinations of dilatation at higher temperatures have earlier been made by Rodwell, and though only used for the position of the transition-temperature, and coincide very well with those above given.

The simple dilatation apparatus used here and with which temperatures between $-180°$ and 0° could be very conveniently obtained, will probably be of some use on other occasions.

§ 3. A detailed examination of our physical knowledge of the critical transformation point A_3 of the iron at about 890° and the lower, more undecided transformation range A_2, *shows that likewise the transformation of the iron at* 890° belongs to Type II: a, of which we thus know two examples. According to this *the nature of the so-called β-iron is to be α-iron* (*stable at low temperatures*) *containing in solution* a limited amount of γ-iron, increasing with the temperature (stable at temperatures above 890°).

This opinion is greatly a returning to the original views of Osmond.

The standpoint now attained simplifies in a high degree our opinion as to the metallography of iron; this is evident from, amongst other things, that the three theories, now acknowledged as the most probable ones, for the constitution of martensite, when seen from this point of view, *become identical.*

It may be added that a recent interesting note by F. Robin, giving the summary of many properties, raises the question whether or not iron has some allotropic transformations at 100–250° and at 400–500°. Also in this case the things will be simpler by taking into consideration the allotropy exposition expounded here: from Robin's paper, it seems probable that iron, at low temperatures, also has an allotropic transformation range of Type IV (Fig. 1) for which T_1 may be about 100°, T_2 about 400–500°.[1]

J. O. Arnold, The physical influence of elements on iron. J. Iron and Steel Inst. 1894: I 107.

J. O. Arnold, II. On a fourth reclescence in steel. (Britt. Ass. Sheffield 1910) Int. Seitschr. f. Metallogr., 192, 1911.

C. Benedicks, Recherches physiques et physico-chimiques sur l'acier au carbone. Upsala, C. J. Lundström: 1904.

C. Benedicks, II. Bemerkungen über die Härte der Metalle und Legierungen. Z. f. phys. Chem. 36, 529, 1901.

C. Benedicks, III. Uber die Härte unde den elektrischen Leitungswiderstand der festen Metalllösungen. Z.f. anorg. Chem. 61, 181, 1909.

[1] Such continuous transformations may also occur in the case of selene, according to R. Marc.

G. Charpy and L. Grenet (Dilatation de l'acier aux hautes temp.) Bull. Soc. pour l'Encouragem. 104, 464, 882, 1903; C. r. 134, 598, 1903.

P. Curie, Propriétés magnétiques des corps. Ann. chim. phys. /4 /5, 289, 1895; Oeuvres, Paris 1908, 232.

R. A. Hadfield, (Discuss. on. magn. properties). U. Inst. Electr. Eng. 1910.

H. M. Howe, The critical ranges in iron and steel. Metallographist 2, 257, 1899.

F. Kohlrausch (Elektr. Best. d. Umwandl.—temp. des AgJ). Wied. Ann. 17, 642, 1882.

H. Le Chatelier, U. Soc. de Phys. 20 Avril 1894.

H. Le Chatelier, II. (Changes of state in iron and steel.) C. r. 1899 Metallographist, 3, 38, 1900.

E. Mallard et H. Le Chatelier (Transf. du AgJ). C. r. 99, 157, 1884.

R. Marc, Die allotropen Formen des Selens. Z. f. anorg. Chem. 48, 393, 1906.

J. Meyer, Die Allotropie der chemischen Elemente. Samml. chem.—chem.—techn. Vorträge 15, 43, 1910.

K. Mönkemeyer (Mischkrist. von AgJ). Diss. Göttingen 1906, 28.

F. Osmond and J. Werth, Théorie cellulaire des propriétés de l'acier Ann. des Mines (8) 8, 5, 1885.

F. Osmond, I. Transformation du fer et du carbone, dans les fers, les aciers et les fontes blanches. Mem. de l'Art. de la Marine 15, 573, 1887.—Paris 1888. II. Etudes métallurgiques. Ann. des Mines (8) 14, 5, 1888. III. On critical points of iron and steel. J. Iron and Steel Inst. 1890:138. IV. Sur la méthode de refroidissement. Comm des Méthodes d'Essai des matériaux de constr. 28 Janv. 1892.

F. Osmond, V. Discussion on Prof. Arnold's paper. J. Iron and Steel Inst. 1894:I, 149.

F. Osmond, VI. Méthode générale pour l'analyse micrographique des aciers au carbone. Bull. Soc. pour l'Encouragem. mai 1895; Contribution à l'Etude des alliages (1901) 277.

F. Osmond, VII. What is the inferior limit of the critical point A_2? Metallographist 2, 169, 1899.

F. Osmond, VIII. (Crystallography of Iron), Ann. des Min. Janv. 1900 Metallographist 3, 181, 275, 1900.

F. Osmond (et G. Cartaud) IX. (Crystallography of Iron). Ann. des Min. Août 1900; Metallographist, 4, 119, 236, 1901.

W. C. Roberts-Austen, Report to the Alloys Research Committee. Min. Proc. Inst. Mech. Eng. 1891, 543.

F. Robin, Die Umwandlüng des Eisens unterhalb 700°. Int. Verb. f. Materialpruf. Kongr. New York 1912, II, 5.

G. F. Rodwell (Dilatation of AgJ) Phil. Trans. 173:3, 1125, 1882.

H. W. B. Roozeboom, die heterogenen Gleichgewichte. Braunschweig 1901.

W. Rosenhain and J. C. W. Humfrey, The crystalline structure of iron at high temperature. Proc. Roy. Soc. A 83, 200, 1909; Phys. Z. 11, 1156, 1910.

G. Tammann (Druckumwandlung von AgJ) Wied. Ann. 68, 558, 1899.

P. Weiss et G. Foëx, Etude de l'aimantation des corps ferromagnétiques au-dessus du point de Curie. Arch. Ici et Nat. Geneve, 4, 31, 4, 89, 1911.

DIE PHYSIKALISCHE NATUR BIOELEKTRISCHER POTENTIALDIFFERENZEN

Reinhard Beutner

Aus dem Rockefeller Institute for Medical Research, New York

Herr Dr. Loeb und der Verfasser haben vor kurzem in dieser Zeitschrift eine Abhandlung betitelt: Uber die Potentialdifferenzen an der unversehrten und verletzten Oberfläche tierischer und pflanzlicher Organe[1], veröffentlicht. In den nachstehenden Zeilen möchte ich eine physikalische Erklärung der in dieser Arbeit gewonnenen experimentellen Ergebnisse zu geben versuchen. Meine Theorie muss sich dabei, soweit sie quantitativ ist, auf die Potentialdifferenzen an der Grenzfläche unversehrter pflanzlicher Organe und wässriger Lösungen beschränken, verletzte Flächen bieten deshalb komplizierte Verhältnisse, weil sie nicht homogen sind.

Der Sitz der bioelektrischen Potentialdifferenzen ist zweifellos an oder in den Membranen zu suchen, d.h. den nicht wässrigen Phasen des Protoplasma welche die Zellen von angrenzenden wässrigen Flüssigkeiten trennen. Dies ist einerseits aus physikalischen Gründen von vorneherein sehr wahrscheinlich und ergiebt sich andererseits aus zahlreichen früheren Untersuchungen.[2] Jede Schnittfläche durch lebendes Gewebe, stellt gewissermassen in elektrischer Bezichung ein Mosaik dar, indem teilweise die Membranen teilweise die wässrigen Flüssigkeiten, die innerhalb und ausserhalb der Zellen sich befinden, zu Tage treten. Eine solche Schnittfläche bietet also in Berührung mit wässrigen Lösungen komplizierte Phänomene: man hat teils Phasengrenzenvon Membran gegen die wässrige Lösungen, teils Grenzflächen der wässrigen Zellularflüssigkeit gegen die wässrige Lösung, und diese beiden Arten von Grenzen verhalten sich elektromotorisch sicherlich sehr verschieden. Ebenfalls komplizierte Verhältnisse bietet die unverletzte tierische Haut, vielleicht auch zum Teil aus anderen Grün-

[1] Biochem. Ztschr. 41, 1 (1912).

[2] Eine Litteratur Zusammenstellung giebt Cremer in Nagels Handbuch der Physiologie. IV Band.

den. Die unverletzte Hülle pflanzlicher Organe dagegen kann als aus einer homogenen wasserunlöslichen Phase bestehend angesehen werden, die Potentialdifferenzen, welche sich an derselben bei Berührung mit wässrigen Lösungen bilden, sind scharf definiert und momentan reversibel.

EXPERIMENTELLE TATSACHEN NACH DER FRÜHEREN ARBEIT

Die experimentelle Untersuchung dieser Potentialdifferenzen, insbesondere ihre Abhängigkeit von der Zusammensetzung der wässrigen Lösung ist in der genannten Arbeit ausführlich beschrieben; sie verdient auch ein gewisses Interesse, denn diese Potentialdifferenzen sind wahrscheinlich gleicher oder ähnlicher Natur wie diejenigen an Membranen innerhalb des Gewebes überhaupt, welche für elektrophysiologische Phänomene der verschiedensten Art verantwortlich, einer direkten physikalischen Untersuchung jedoch nicht zugänglich sind.

Ich möchte daher die untersuchten Potentialdifferenzen der Kürze halber als bioelektrische (abgekürzt b. D. P.) bezeichnen. Das für die folgende Untersuchung wichtigste Resultat der früheren bezüglich derselben kann folgendermassen zusammengefasst werden.

Die b. T. D. (an Grenze einer unverletzten Pflanzenteils gegen die wässrige Lösung eines Alkali — oder Erdalkalisalzes) ist von der *Konzentration der Lösung in der Weise abhängig, dass Verdünnung der Lösung dieselbe positiver macht.* Alle Alkali und Erdalkalisalze und auch alle anderen Elektrolyte zeigen ein solches Verhalten, soweit sie nicht stark giftig, d. h. chemisch verändernd auf die Oberfläche der Pflanze einwirken. Die Anderung der Potentialdifferenz ist in dem gleichen Sinne, diejenige an der Phasengrenze Beliebiges Metall | Metallsalzlösung wechselnder Konzentration. Man kann also sagen, dass die b. P. D. *für Kationen reversibel sind,* und zwar *in merkwurdigem Gegensatz zu den bisher bekannten Potentialen für Kationen jeder Art.* Die Grösse der Anderung ist in einem gewissen Konzentrationsbereich beinahe so gross wie nach der Nernst'schen Formel für Potentialdifferenzen $\left(E = \frac{RT}{nF} \ln c + \text{const.}\right)$ zu erwarten ist. Geht man von kleinen Konzentrationen der Salzlösung, etwa 1/1000 molekular, aus und erhöht die Konzentration stufenweise in geometrischer Reihe, z. B. durch Verdoppelung, so findet man dass die Veränderung der b. P. d. etwa 0.058 lg 2 ist bis die Konzentration auf etwa 1/50 mol. gestiegenist; über 1/50 mol. wird die Anderung erheblich kleiner, ist die Konzentration auf 1/2 bis 1/1 mol. gestiegen, so hat weitere Erhöhung keinen Einfluss. *Mit steigender Konzentration strebt also die b. P. D. einem Grenzwert zu.*

SCHEINBARE ABWEICHUNG VOM NERNST'SCHEN GESETZ BEI KLEINEN KONZENTRATIONEN

Erniedrigt man die Konzentration unter 1/1000 molek. so findet man ebenfalls Abweichungen von der Nernst'schen Formel. Diese Abweichungen sind indes nur scheinbar und dem Umstande zuzuschreiben, dass bei Konzentrationen von 1/1000 bis 1/100000 molekular die elektrolytischen Verunreinigungen des destillierten Wassers mit ins Spiel kommen. Das zu diesen Versuchen benutzte destillierte Wasser hatte schätzungsweise nach seiner Leitfähigkeit einen Ionen Gehatt von 1/10000 bis 1/100000 wechselnd. (Eine weitere sorgfältige Reinigung hatte keinen Zweck, da in Berührung mit der Blatt-oder Frucht Oberfläche stets eine Erhöhung der Leitfähigkeit erfolgte.) Da bei den b. P. D. alle Elektrolyte in gleichem Sinne bei Konzentrationsänderung wirken, kann auch die Wirkung der verunreinigenden Ionen nicht vernachlässigt werden. Kontrolliert man durch Leitfähigkeitsbestimmungen die wahren Ionen Konzentrationen, so findet man die Nernst'sche Formel bis zu den höchsten Verdünnungen bestätigt, wie folgendes Beispiel zeigt. Die Kette.

Kalomel Elektrode 1/10 n KCl | Apfel $\underset{a}{|}$ 1/500 KCl Kalomel Elektrode zeigte die E.M.K. 0.064 Volt (2^{1} konstant). Wurde die 1/500 KCl — Lösung durch eine 1/1000 n KCl — Lösung ersetzt so war die E.M.K., entsprechend der Anderung der b. P. D. bei *a* 0.082 Volt Diff.: 0.018 Volt, nach Nernst's Formel ber, 0.058 lg 2=0.0175 Volt, also vorzügliche Ubereinstimmung. Leitfähigkeitsbestimmungen ergaben, dass die Konzentration der Lösung durch Verunreinigungen nicht beeinflusst war. Wurde darauf die Konzentration der KCl — Lösung bei *a* durch fünf fache Verdünnung auf 1/5000 erniedrigt, so war die E.M.K.: 0.110 Volt, Differenzen gegen 1/1000 n KCl, 0.028 Volt, Nernst's

Formel giebt 0.058 lg 5=0.040 Volt. Diese Abweichung wird verständlich durch Messung der Leitfähigkeit der scheinbar 5000 n KCl — Lösung. $K_2|^\circ$ gemessen 0.0000378, berechnet nach Kohlrausch 0.0000258. Nimmt man an, dass die verunreinigenden Ionen bezüglich Wanderungsgeschwindigkeit sich wie das KCl verhalten, so wäre die wahre Konzentration der 1/5000 n KCl — Lösung $\frac{378}{258}\cdot\frac{1}{5000}=\frac{1}{2940}$, Differenzen der E. M. KK. bei 1/1000 und 1/2940:

$$0.058 \lg 2.94 = 0.0272 \text{ Volt Gefunden } 0.028 \text{ Volt.}$$

Diese scheinbare Abweichung hat hiernach mit besonderen Eigentümlichkeit der b. P. D. nichts zu tun, ist vielmehr nur ein anderer Ausdruck der Tatsache, dass alle Kationen die b. P. D. im gleichen Sinne Beeinflussen. Anders liegt es bei den Abweichungen von der Nernst'schen Formel bei hohen Konzentrationen. Diese können nicht etwa durch Zurückgehen der elektrolytischen Dissoziation bei hohen Konzentrationen erklärt werden. Der Grenzwert der b. P. D. wird bei einer Konzentration von 1/2 mol. bis 1/1 mol. erreicht, auch bei weiterer Konzentrationssteigerung muss aber die absolute Ionen Konzentration offenbar trotz des Zurückgehen des Dissoziationgrades steigen. Die Unveränderlichkeit der b. P. D. in diesem Gebiete zeigt, dass besondere Eigentümlichkeiten der Membran in Spiel sind.

ELEKTROMOTORISCHES VERHALTEN VON SYSTEMEN MIT ZWEIN UNMISCHBAREN ELEKTROLYTISCHEN PHASEN

Das Zustandekommen von Potentialdifferenzen, wie der b. P. D., kann Physikalisch auf zwei verschiedenen Wegen erklär werden. Auf jeden Fall ist es Voraussetzung, dass eine wasserunlösliche Phase (in diesem Falle die Schale oder Membran des Pflanzenteils) neben wässriger Lösung von Bedeutung ist. Es seien zunächst die allgemeinen physikalischen Tatsachen über das Zustandekommen von Potentialdifferenzen in Systemen mit zwei elektrolytischen Phasen besprochen.

Nernst hat zuerst das elektromotorische Verhalten von Systeme mit zwei unmischbaren Phasen experimentell und theoretisch untersucht. Gemeinsam mit Riesenfeld[1] untersuchte er Anordnungen wie.

Verdünnte wässrige Lösung eines beliebigen Salzes z.B. $AgNO_3$	Phenol	Konzentrierte wässriege Lösung desselben Salzes ($AgNO_3$)
1		2

Zwei Arten von Potentialdifferenzen sind in diesen Ketten zu unterscheiden.

1. *"Diffusionspotentiale" in dem Phenol.* Diese kommen zu Stande, wenn die betreffenden Salze eine erhebliche Löslichkeit in dem Phenol besitzen, so dass *die Stromleitung durch die Phenolschicht vermittels der gelösten Salze, resp. deren Ionen, vor sich geht.* Unmittelbar an den Phasengrenzen 1 und 2 besteht nun Verteilungs — Gleichgewicht, das Phenol enthält bei 1 eine kleine, bei 2 eine grosse Konzentration an $AgNO_3$. In der Phenolschicht besteht also ein Konzentrations-Abfall, die Anderung des Potentials längs desselben ist gegeben durch die Funktion:

$$\frac{u-v}{u+v}\,\frac{R\,T}{n\,F}\ln\frac{{}^{c}2}{{}^{c}1}.$$

In wässrigen Lösungen sind u und v meist ungefähr gleich gross und deshalb die Diffusionspotentiale stets klein, in dem Phenol liegen ähnliche Verhältnisse vor. Nimmt man jedoch an, dass in manchen nicht wässrigen Phasen wie z. B. den Membranen erhebliche Unterschiede in der Wanderungsgeschwindigkeit der positiven und negativen Ionen bestehen, so könnte die Art von Abhängigkeit der b. P. D. von Konzentrationen, wie sie hier beschrieben ist, auftreten. Ist z. B. v in der Membran gleich Null, so wäre das Diffusionspotential gleich $\frac{R\,T}{n\,F}\ln\frac{{}^{c}2}{{}^{c}1}$. Ich möchte jedoch diese Deutung aus folgenden Gründen für nicht sehr wahrscheinlich halten.[1]

Die Erklärung setzt voraus, dass die Stromleitung durch die zweite Phase (Membran) *ausschliesslich* durch die Salze, welche aus der wässrigen Lösung in die Membran eintreten, vor sich geht. Nun sind wie sich aus osmotischen Versuchen ergiebt die Membranen sehr schwer durchgängig für Salze. Nur äusserst geringe Salzspuren dringen also in die Membrane selbst unter den günstigsten Bedingungen, d. h. wenn die Salzlösung am konzentriertesten ist, ein. Die Leitfähigkeit der Membran müsste durch diese Salzspuren bedingt sein und würde auf Null zurückgehen, wenn die Membran nur mit Wasser umspült ist. Dies ist im hohen Grade unwahrscheinlich, die Membran besitzt wahrscheinlich einen sehr geringen Gehalt an elektrolytischen Ionen, welche unabhängig von den *eingedrungenen ist, und da die Konzentration der letzteren sehr gering ist,* NICHT *neben ihnen vernachlässigt werden kann.*

---

[1] Nernst u. Riesenfeld, Annaben der Physik, *8*, 600 to 609.

Ferner ist es mit dieser Annahme kaum verständlich, weshalb die b. P. D. bei hoher Konzentration einem Maximum zustreben, es müssten weitere komplizierte Hilfsannahmen zu diesem Zweck gemacht werden; dabei hat die Annahme extrem differenzierter Ionen Wanderungsgeschwindigkeiten schon an und für sich einen stark hypothetischen Charakter. Ich glaubte diese Erklärungsmöglichkeit hier nur deshalb diskutieren zu müssen, da physiologische Forscher den Verletzungsstrom auf diese Art zu erklären versucht haben. Auch diesen Theorien ist eine gewisse Unsicherheit kaum abzusprechen.

Die andere Art von Potentialdifferenzen, welche in der Nernst-Riesenfeld'schen Kette möglich ist, hat ihren Sitz an der *Phasengrenze selbst.*

Nernst[1] selbst hat vor längerer Zeit gezeigt, dass Phasengrenzpotentiale zwischen elektrolytischen Leitern in derselben Weise wie Potentiale an Metal-Elektrolytgrenzen von der Ionen Konzentration abhängig $= \frac{RT}{nF} \ln \frac{c_1}{c_2} + \text{const.}$, wo c_1 resp. c_2 die Konzentration eines beliebigen *beiden Phasen gemeinsamen Ion in den beiden Phasen bedeutet. Diese für die Elektrochemie fundamentale Tatsache beweist man am besten mit Hilfe einer fiktiven Kette wie*

Metall		Phase I Salz des Metalles enthaltend		Phase II Salz des Metalles enthaltend		Metall
	1		2		3	

Die Phase I und II sowie das Metall befinden sich im Gleichgewicht und somit ist irgend eine chemische (oder physikalische) Reaktion in einer solchen Anordnung nicht möglich, auch nicht bei Stromfluss durch das System. *Die Summe der drei Potentialdifferenzen bei 1, 2 und 3 muss somit gleich Null sein.*

---

[1] Nernst, Zeitschr. physik. Chem. *9*, 137, 1892.

Da Pot. Diff. bei $1 = \frac{RT}{nF} \ln c_1 + \text{const.}_1$

und Pot. Diff. bei $3 = \frac{RT}{nF} \ln c_2 + \text{const.}_2$ in entgegengesetzer Richtung so ergiebt sich

für P.D. bei $2 = \frac{RT}{nF} \ln \frac{c_1}{c_2} + \text{const.}_1 - \text{const.}_2$

In einer Kette wie der Nernst-Riesenfeld'schen kommt diese Abhängigkeit des Phasengrenzpotential von der Konzentration nicht zum Vorschein, weil $AgNO_3$ in Wasser und Phenol löslich ist und das Phenol keinen weiteren Elektrolyten enthält.

Für das Dissoziationsgleichgewicht im Wasser gilt:

$$C_{Ag^{\cdot}} C_{NO_3'} = K_1 C^n_{AgNO3}$$

Für das Dissoziationsgleichgewicht im Phenol gilt:

$$C_{Ag}.C_{NO_3'} = K_2 C^n_{AgNO_3}$$

Nach dem Verteilungssatz gilt, da an der Phasengrenze selbst stets Gleichgewicht herrschen muss:

$$\frac{C_{AgNO3}}{C_{AgNO3}} = K_3$$

Division der beiden ersten Gleichungen gibt:

$$\frac{C_{Ag^{\cdot}}}{C_{Ag^{\cdot}}} . \frac{C_{NO_3'}}{C_{NO_3'}} = \frac{K_1}{K_2} . K_3 = K$$

$$\text{Da} C_{Ag^{\cdot}} = C_{NO_3^1} \text{ und } C_{Ag^{\cdot}} = C_{NO_3^1},$$

$$\frac{C^2_{Ag^{\cdot}}}{C^2_{Ag^{\cdot}}} = K \qquad \frac{C_{Ag^{\cdot}}}{C_{Ag^{\cdot}}} = \sqrt{K}.$$

Das Phasengrenzpotential ist also: $\frac{RT}{nF} \ln \sqrt{K} + \text{const.}$ d.h. von der Ag = Konzentration unabhängig. Eine Konzentrationserhöhung im Wasser bringt eben eine solche im Phenol mit sich, und das Verhältnis $\frac{C_{Ag}}{C_{Ag}}$, auf das es für die Potentialdifferenzen ankommt, bleibt unverändert. Dies ist auch der Fall, wenn der Elektrolyt in der einen Phase weitgehender als in der anderen dissoziiert ist, vorausgesetzt, dass das Verteilungsgesetz in der hier angewandten einfachen Form gilt. Anders verhält es sich, wenn die Ionen Konzentrationen der beiden an einandergrenzenden Phasen sich nicht gegenseitig beeinflussen. Dies ist z. B. der Fall in der von Haber[1] zuerst untersuchten Potentialdifferenz

$$\begin{array}{c|l} \text{AgCl} & \\ \text{fest} & \text{AgNO}_3\text{—Lösung oder allgemein} \end{array}$$

$$\begin{array}{r|l} \text{Unlösliches Salz} & \text{Lösung eines Salzes mit} \\ & \text{einem gleichen Ion.} \end{array}$$

Die Ag Konzentration in der Schicht des festen AgCl ist natürlich völlig unabhängig von der Ag Konzentration der wässrigen Lösung. Nach der Nernst'schen Formel ist die Potentialdifferenz gleich zu setzen

$$\frac{\text{R T}}{\text{n F}} \ln \left(\frac{C_{Ag^{\cdot}} \text{ in } A_gCl}{C_{Ag^{\cdot}} \text{ in } A_gNO_3 \text{ Lösung}} \right) + \text{const.}$$

da $C_{Ag^{\cdot}}$ im AgCl konstant bleibt, folgt somit, dass diese Potentialdifferenz sich wie eine solche an einer metallischen (Ag) Elektrode ändert, was sich experimentell bestätigen liess. Die Phasengrenzformel ist so einer direkten Prüfung zugänglich.

ANWENDUNG DER PHYSIKALISCHEN ERGEBNISSE AUF DIE B. P. D.

Die b. P. D. verhalten sich nun im Gebiet der kleinsten Konzentrationen 1/100 n und weniger wie die Phasengrenzpotantiale vom Typus AgCl | $Ag^{\cdot}$ haltige wässrige Lösung, im höchsten Konzentrationsgebiet (ca. 1/2 n oder mehr) wie die Phasengrenzpotentiale der Nernst-Riesenfeld'schen Kette. Das dazwischen liegende mittlere Konzentrationsgebiet verhält sich wie eine Ubergangszone zwischen diesen beiden Extremen.

Eine befriedigende Erklärung dieses Verhaltens gelingt mit Hilfe der Annahme, dass die Membran einen *Eigengehalt an Elektrolyten* besitzt, d.h. wasserunlösliches Salz in homogener Mischung enthält. Ferner nehemen wir an, dass die Alkali-Salze in der Membran eine kleine, aber endliche Löslichkeit besitzen.

Es sei das wasserunlösliche Salz in der Membran mit Y X bezeichnet (Y^1Anion, X^1Kation), die wässrige Lösung enthalte KCl als Elektrolyt. Ferner nehmen wir an, dass YX mit dem in die Membran eingedrungenen KCl, nach einer vollständig verlaufenen Gleichung reagiert etwa so, dass elektrolytisch dissoziiertes KX und undissoziiertes Y Cl entsteht.

---

[1] *Haber*, Ann. d. Physik [4] *26*, 947 (1908). An dieser Arbeit war der Verfasser eben falls beteitigt.

$YX + KCl \rightarrow KX + YCl$

weitgehend wenig oder im Wasser leicht löslich, so
dissoziiert dissoziiert dass es aus der Membran ausgelaugt wird.

Oder es könnte folgender Umsatz stattfinden:

$YX + KCl \rightarrow YX\,Cl\,K$

Diese Additionsverbindung sei in die elektrolytischen Ionen YX Cl^1 einerseits, K^1 andererseits dissoziiert (also in derselben Weise wie Platinchlorid-doppelsalze). Beide Annahmen sind für unseren Zweck gleichwertig; sie sind geboten angesichts der Tatsache, dass die Reversibilität der b. P. D. gegenüber *allen* Kationen besteht.

Diese Annahme vom Umsatz gewisser Bestandteile des Gewebes mit Salzen in wässriger Lösung ist übrigens durchaus nicht völlig neu, vielmehr in ähnlicher Weise auf Grund ganz anderer Beobachtungen vor langer Zeit schon von J. Loeb ausgesprochen worden. Loeb beobachtete, dass die Reizbarkeit sowie die rhytmische Bewegung von Muskeln in gemischten Salzlösungen reversible, von der Natur des *Kations* abhängige Anderung erfuhr; z. B. hebt Zusatz von sehr geringen Mengen von Ca^1 zu Na$'$-Lösungen die rhytmischen Bewegungen auf, ähnliche reversible Wirkungen lassen sich mit Anionen *nicht* beobachten. *Loeb*[1] "stellte sich deshalb vor, dass die Metalle oder Metallverbindungen in den Geweben mit bestimmten organischen Stoffen wie festen Säuren oder Eiweisskörpern verbunden sind, und dass die Substitution eines Metalles für ein anderes die physikalischen Eigenschaften dieser Verbindungen ändert, z. B. Oberflächenspannung, die Viskosität, das Wasserabsorptionsvermögen und den Aggregatzustand. Die Lebenserscheinungen und die Erscheinungen der Reizbarkeit hängen davon ab, dass gewisse Eiweissverbindungen oder Metallseifen in bestimmten Verhältnissen in den Geweben vorhanden sein müssen."

Diese Annahme wird durch die Resultate der vorliegenden Arbeit vollauf bestätigt, obgleich dieselben auf einem wesentlich anderen Gebiet liegen.

[1] Dynamik der Lebenserscheinungen, p. 120.

Ferner ist folgende für die Theorie vereinfachende Schlussfolgerung geboten. Bei genügend verdünnter Lösung ist, wie wir gesehen haben, die Nernst'sche Formel für b.P.D. innerhalb eines weiten Konzentrationsgebietes in der gleichen Weise wie für Elektrodepotentialdifferenze gültig, nämlich b.P.D. $= \frac{RT}{nF}$ lnC nüppr. Lösung + const.

Dies ist mit der gemachten Annahme nur dann zu vereinigen, wenn der Umsatz nach irgend einem der genannten Schema vollständig vor sich geht, das heisst, von der Konzentration des Salzes in der wässrigen Lösung im wesentlichen unabhängig ist. Nach dem Verteilungssatz ist andererseits die Konzentration des KCl in der Membran, von der wässrigen KCl Konzentration abhängig, und wir nehmen an, dass das Verteilungsgesetz in der einfachsten Form gilt, dass also Proportionalität der wässrigen und der Membran-Konzentration besteht.

Bei kleinen wässrigen Konzentrationen ist die KCl Konzentration in der Membran so klein, dass sie neben der K^1 Konzentration, welche durch den Elektrolyt-Eigengehalt der Membran bedingt ist, vernachlässigt werden kann. Offenbar ist hiermit die Bedingung einer Veränderlichkeit der b. P. D. nach der Art der Potentialdifferenz AgCl | Ag^1-Lösung gegeben. Bei den höchsten wässrigen Konzentrationen dagegen steigt die KCl-Konzentration der Membran so weit, dass nunmehr umgekehrt der K^1 Eigengehalt der Membran vernachlässigt werden kann; das würde offenbar eine Veränderlichkeit der b.P.D. nach Art der Potentialdifferenz $AgNO_3$ in Phenol | $AgNO_3$ in Wasser zur Folge haben, wie sie tatsächlich beobachtet wird.

ANALYTISCHE FORMULIERUNG DER BESCHRIEBENEN HYPOTHESE

Zur Darstellung der gegenseitigen Abhängigkeit der Ionen Konzentrationen in Membran und wässriger Lösung benutzen wir die üblichen und bewährten Vorstellungen der elektrolytischen Dissoziation und des beweglichen Gleichgewichts.

Membran Wasser c bezeichne Konzmetrationen in wässriger Lösung.
$KX = K^1 + X'$
$KCl = K^1 + Cl^1$
$KCl = K^1 + Cl^1$ C Konzentrationen in der Membran.

Wir nehmen an, dass für die elektrolytische Dissoziation des KCl in Wasser und Membran des Massenwirkungsgesetz in der gleichen Weise angesetzt werden kann, nämlich:

$$C_{K\cdot} C_{Cl}' = K_1 C_{KCl}{}^{n1}$$

also entsprechend

$$C_{K\cdot} C_{Cl}' = K_2 \, C_{KCl}{}^{n}$$

(Die Konstanten K_1 und K_2 sollen nicht gleich sein, wohl aber die Exponenten von C_{KCl} und $C_{KCl\cdot}$.)

Das Verteilungsgesetz setzen wir an in der einfachen Form:

$$\frac{C_{KCl}{}^{\cdot}}{C_{KCl}} = K_3$$

Division der beiden ersten Gleichungen und Substitution mittels der dritten ergiebt:

$$\frac{C_K}{K} = \frac{K_1}{K_2} \cdot \frac{1}{K_3} \, \frac{C_{Cl}'}{C_{Cl}'}$$

$$= \frac{1}{K} \, \frac{C_{Cl}'}{C_{Cl}'} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{I}$$

Nach der Regel der Elektroneutralitat ist

$$C_{K\cdot} = C_{Cl}' = C \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{II}$$

$C_{K\cdot} = C_{Cl}' + C_X$[1]

oder $C_{Cl\cdot} = C_{K\cdot} - C_{Cl}' \ldots\ldots\ldots\ldots\ldots\ldots \text{III}$

II und III substituiert in I giebt

$$\frac{C}{C_{K\cdot}} = \frac{1}{K} \cdot \frac{C_{K\cdot} - C_X'}{C}$$

$$C_{K\cdot}^2 - C_X' C_{K\cdot}^X = K\,C^2$$

$$C_{K\cdot} = \frac{C_X'}{2} \pm \sqrt{\frac{C_X'^2}{4} + K\,C^2}$$

Von den beiden Lösungen der quadratischen Gleichung hat nur die jenige mit positivem Vorzeichen vor der Wurzel einen physikalischen Sinn. Da nämlich K sowohl als auch C^2 nie einen negativen Wert annehmen können, muss der Wert der Wurzel notwendigerweise grösser als $\frac{C_X'}{2}$ sein; bei negativem Vorzeichen würde dies bedeuten, dass $C_{K\cdot}$, eine Konzentration, negativ ist, eine physikalische Unmöglichkeit! Es ist also

---

[1] Dies ist die Empirische Form des Massenwirkungsgesetzes (oder Verdünnungsgesetzes) nach van't Hoff und Rudlolphi.

$$C_{K\cdot} = \frac{C_X{}'}{2} + \sqrt{\frac{C_X{}'^2}{4} + KC} \ldots\ldots \quad \ldots \text{IV}$$

Nach der zitierten Nernst'schen Formel ist die b. P. D. =

$$\frac{R\,T}{n\,F} \ln \frac{C_K}{C_K} + \text{const. oder } \frac{R\,T}{n\,F} \ln \frac{C_K}{C} + \text{const.}$$

Substituiert man für $C_{K\cdot}$ den Wert aus (IV so ergiebt sich

$$\text{b.P.D.} = \frac{RT}{n\,F} \ln \frac{C_{X'}}{2c} + \sqrt{\frac{C_{X'}^2}{4c^2} + K} + \text{const} \ldots\ldots\ldots \text{V.}$$

Halten wir an unserer Annahme fest, dass die elektrolytische Dissoziation in der Membran ähnlich der in Wasser ist, so kann C_X in erster Annäherung als unabhängig von C (wäss. Konz.) angesehen werden. KX wäre dann nämlich weitgehend dissoziiert und die Zurückdrängung, der Dissoziation durch überschüssiges KCl sehr gering; obgleich die KCl-Konzentration der Membran sich mit c ändert, bliebedie Dissoziation von KX doch unbeeinflusst: C_X ist von C unabhängig.

Unter Berücksichtigung dieser Verhältnisse giebt die Gleichung V den charakteristischen Verlauf der b. P. D. gut wieder. Wir betrachten zunächst die Grenzbedingungen.

(1) Sehr kleine wässrige Konzentrationen.—Die Gültigkeit der Nernst'schen Formel in der einfachsten Form kommt bei sehr kleinem c; offenbar dadurch, dass K neben $\left(\frac{C_X}{2c}\right)^2$ vernachlässigt-werden kann. Gleichung V nimmt danndie Form an

$$\text{b.P.D.} = \frac{RT}{nF} \ln \frac{C_X}{c} + \text{const.}$$

$$\text{oder} = \frac{R\,T}{n\,F} \ln \frac{1}{c} + \text{const.}^{1}$$

d.h. die b. P. D. ändert mit c wie eine Elektroden-Potentialdifferenz.

(2) Sehr grosse wässrige Konzentrationen.—In diesem Falle kann umgekehrt $\left(\frac{C_X}{2c}\right)^2$ neben K vernachlässigt werden. Die Formel V nimmt die einfache Gestalt an

$$\text{b. P. D.} = \frac{RT}{nF} \ln \sqrt{K} + \text{const.}$$

d.h. bei hohen Konzentrationen ist die b.P.D. von c unabhängig.

Das experimentum crucis für die Brauchbarkeit unserer Theorie bieten jedoch *die mittleren Konzentrationen,* denn offenbar können die Grenzbedingungen auch durch eine einfache empirische Gleichung wie z. B.

$$\text{b.P.D.} = \frac{R\,T}{n\,F} \ln \left(\frac{1}{c} + K\right) + \text{const.}$$

zum Ausdruck gebracht werden. Die Art und Weise, mit der die b.P.D. vom Grenzwert bei hohen Konzentrationen absinkt, wenn die Lösung stufenweise verdünnt wird, muss experimentell mit den Forderungen der Theorie verglichen werden. Zwecks empirischer Prüfung der Gleichung V. müssen die Konstanten, C_X und K, zunächst empirisch bestimmt werden. Eine einzige Bestimmung ist wie die folgenden Ableitungen zeigen, hierfür genügend. Mathematisch am einfachsten ist es, als empirische Differenz diejenige bei $C = 1/500$ normal und der Grenz E.M.K. bei sehr grossem c zu wählen. Es gilt dann bei Zimmertemperatur

$$\text{E.M.K.}_{\text{bei } c=1/500} = 0.058 \ \underline{\lg} \ (250 \ C_X + \sqrt{250^2 C_X^2 + K}) = \text{const.}$$

$$\text{E.M.K.}_{\text{limit}} = 0.058 \lg \sqrt{K} + \text{const.}$$

Differenz: $\text{E.M.K.}_{c = 1/500} - \text{E.M.K.}_{\text{limit}} =$

$$0.058 \lg \frac{250 C_X + \sqrt{250^2 C_{X_2} + K}}{\sqrt{K}}$$

Diese Differenz setzen wir gleich 0.058 lg 1/m, wo m also eine experimentell zu bestimmende Grösse ist.

Es folgt

$$250 \ C_X + \sqrt{250^2 C_X^2 + K} = \frac{1}{m}\sqrt{K}$$

Auflösung dieser Gleichung nach $\sqrt{K}$:

$$\sqrt{250^2 C_X^2 + K} = \frac{1}{m}\sqrt{K} - 250 C_X$$

quadriert: $$+K = \frac{1}{m^2} K - 500 \ \frac{1}{m} \sqrt{K} \ C$$

mit $\sqrt{K}$ dividiert: $$\sqrt{K} = \frac{1}{m^2}\sqrt{K} - 500 \frac{1}{m} C_X$$

$$-\sqrt{K}+\frac{1}{m^2}\sqrt{K}=500\frac{1}{m}C_X$$

$$\sqrt{K}=\frac{500\,C_X}{m\left(\frac{1}{m^2}-1\right)}$$

Berücksichtigt man, dass lg 1/m gewöhnlich etwagleich 2 ist, $\frac{1}{m^2}$ also circa 10000, so kann statt $\frac{1}{m^2}-1$ geschrieben werden $\frac{1}{m_2}$. Für $\sqrt{K}$ ergiebt sich dann näherungsweise

$$\sqrt{K}=500\ m\ C_X.$$

Dieser Wert in V substituiert giebt für

$$b.\,P.\,D.=\frac{RT}{nF}\ln\left(\frac{C_X}{2c}+\sqrt{\frac{C_X^2}{4c^2}+500^2{}_m{}^2C_X{}^2}\right)+\text{const.}$$

Die Differenz zweier beliebigen E.M.KK., die sich nur durch die Konzentrationen c_1 resp. c_2 an der Grenze der Membran unterscheiden, ist also

$$E_{c1}-E_{c2}=0.058\log\frac{\frac{C_X}{2_{c1}}+\sqrt{\frac{C_X^2}{4_c{}^2}+500^2{}_m{}^2C_X{}^2}}{\frac{C_X}{2_{c2}}+\sqrt{\frac{C_X^2}{4_c{}^2{}_2}+500^2{}_m{}^2C_X{}^2}}$$

Wie man sieht hebt sich C_X aus dem Quotient hinter dem log heraus; wird der Quotient ausserdem mit 2 erweitert, so ergiebt sich:

$$E_{c1}-E_{c2}=0.058\log\frac{\frac{1}{c_1}+\sqrt{\frac{1}{c_1^2}+1000^2{}_m{}^2}}{\frac{1}{c_2}+\sqrt{\frac{1_2}{c_2}+1000^2{}_m{}^2}}$$

$$=0.058\log\frac{\frac{1}{c_1}.\left(1+\sqrt{1+10^6{}_{m2c1}{}^2}\right)}{\frac{1}{c_2.}\left(1+\sqrt{1+10^6{}_m{}^2{}_{c2}{}^2}\right)}$$

$$E_{c1}-E_{c2}=0.058\ \log\frac{c_2}{c_1}-0.058\ \log\frac{1+\sqrt{1+10^6{}_m{}^2C_2^2}}{1+\sqrt{1+10^6{}_m{}^2C_1^2}}$$

m war oben definiert durch die Beziehung

$$\log\frac{1}{m}=\frac{E_{c=\frac{1}{500}}-E_{\text{limit}}}{0.058}$$

EXPERIMENTELLE PRÜFUNG DER THEORIE

Diese Formel gilt, wenn KCl als Elektrolyt zugegen ist oder auch bei irgend einem anderen binären einwertigen Elektrolyten; für zwei wertige Elektrolyte wie $CaCl_2$ lässt die Theorie eine kompliziertere Beziehung voraussehen. Die experimentelle Prüfung geschieht durch Messung der E.M.K. von Ketten wie.

Kalomel Elektrode	Apfel oder Blatt	Lsöaung vriabler Zusammensetzung	Kalomel Elektrode
	a	b	

In dieser Kette ist ausser der b.P.D. bei *a* durch dasDiffusionspotential bei *b* von der Konzentration der variablen Lösung abhängig. Bei *KCl* als *Elektrolyt* in der variablen Lösung sowie in der Kalomelelektrode (konstant 1/10 n) kann das Diffusionspotential bei *b* als unveränderlich angesehen werden, und es sind deshalb solche Versuche zur Prüfung der Theorie besonders geeignet.

1. Versuchsreihe beim Apfel (KCl als Elektrolyt)

Gemessen bei $c=\frac{1}{500}$n KCl: 0.0874 Volt

Gemessen bei $c=\frac{1}{n}$ oder $\frac{1}{2}$ n KCl: —0.0220 Volt Dies kann als dem Grenzwert der b.P.D. entsprechend angesehen werden.

Es ist somit $\log\frac{1}{m}=\frac{0.1094}{0.058}=1.8862$

$$\lg\ m^2=-3.7724$$

$$10^6\,m^2=217.6$$

$$Ec_2-Ec_1=58\lg\frac{c_2}{c_1}-58\lg\frac{1+\sqrt{1+21F_6C_2^2}}{1+\sqrt{1+21F_6C_1^2}}$$

(in Milli Volt)

Kohzentrations-Intervall	Berechnet (Milli Volt)	Beobachtet bei zunehmender Konzentration	Beobachtet bei abnehmender Konzentration	Mittel
1/1 bis 1/2	1.5		1	1
1/2 bis 1/4	3.0	6.7	3.0	4.9
1/4 bis 1/8	6.0	9.6	6.0	7.8
1/8 bis 1/16	10.5	8.9	11.3	10.1
1/10 bis 1/20	12.0	13.2	12.8	13.0
1/20 bis 1/40	15.0	15.6	12.8	14.4
1/40 bis 1/80	17.0	16.0	14.7	15.3
1/2 bis 1/40	12.6	19.0	21.0	20.0
1/4 bis 1/20	21.0	15.5	26.5	21.0
1/8 bis 1/40	30.0	32.0	30.0	31.0
1/16 bis 1/80	36.6	38.6	35.0	36.8

Wie man sieht, sind bei Anderung der Konzentration in entgegengesetzter Richtung die Anderungen der E.M.K. nicht völlig gleich, besonders bei hohen Konzentrationen besteht diese Unsicherheit. Angesichts dieser mangelhaften Reversibilität kann die Ubereinstimmung mit der Theorie als befriedigend angesehen werden, die Abweichungen der beobachteten Mittelwerte von den berechneten sind nur in einem Falle grösser als 2 Milli Volt (Intervall 1/2 bis 1/40), in den übrigen zehn Fällen kleiner. Eine grössere Genauigkeit als 2 Milli Volt kann bei solchen Messungen nicht erzielt werden. (Die Messung geschah n. b. mit einem empfindlichen Spiegelelektrometer.)

Eine weitere Versuchsreihe wurde ebenfalls am Apfel mit KCl ausgeführt, wobei die Konzentrationsintervalle andere waren.

Gemessen bei $c=\frac{1}{500}$ KCl 0.0750 Volt

Gemessen bei $c=\frac{1}{1}$ KCl -0.0294 Volt

Es ist somit $\lg\frac{1}{m}=\frac{0.1046}{0.058}=1.8034$

$10^6 m^2=247.28$

Konzentrations-Intervall	Berechnet (Milli Volt)	Beobachtet
1/500 n bis 1/250 n	17.5	17
1/250 n bis 1/125 n	17.0	15.2
1/125 n bis 1/25 n	38.5	36.3
1/50 n bis 1/25 n	16	16
1/25 n bis 1/5 n	23.5	27
1/5 n bis 1/1 n	6.5	8
1/1 n bis 2 1/2 n	1	1 in entgegengesetzter Richtung

Auch bei diesen Versuchen ist die Ubereinstimmung befriedigend.

Messungen der gleichen Art wie die eben beschriebenen mit dem *Blatt einer Gummipflanze* (ficus elastica) sind in der genannten früheren Arbeit gegeben. Ich möchte auch für diese Messungen die hier abgeleitete Formel prüfen.

Konzentrations-Intervall	Beobachtet (Milli Volt)				
	I	II	III	Mittel	Berechnet
1/1250 bis 1/250	31	33	35	33	40
1/250 bis 1/50	30	32	31	31	36.5
1/50 bis 1/10	23	31	21	23	18.5

Zur Ausführung der Berechnung war Kenntnis des Grenzwertes der Kraft, welcher bei noch höherer Konzentration erreicht wird erforderlich. Es wurde in besonderen Versuchen gefunden

Konzentrations-Intervall		Die Berechnung ergab
1/10 n bis 1/2 n	Milli-Volt	Milli-Volt
1/2 n bis 5/2 n	Milli-Volt	Milli-Volt

Was die Berechnung für diese Beispiele betrifft, so wurde hier soverfahren, dass die Grösse m definiert wurde durch die Beziehung

$$\log\frac{1}{m}=\frac{E_{C=\frac{1}{250}}-E_{\text{limit}}\,(2\tfrac{1}{2}n)}{0.058}$$

Entsprechend lautet die Hauptformel:

$$E_{C_2}-E_{C_1}=58\log\frac{C_2}{C_1}-58\log\frac{1+\sqrt{1+500^2m^2C_2^2}}{1+\sqrt{1+500^2m^2C_1^2}}$$

(Milli Volt)

In derselben Weise möchte ich auch Versuche mit NaCl-Lösungen verschiedener Konzentration, welche sich in der früheren

Arbeit angegeben sind durchgerechnen. Bei diesen Experimenten ist jedoch zu beachten, dass in der entsprechenden Kette

Kalomel Elektrode	Blatt des Gummibaums	NaCl-Lösung wechselnder Konzentration	Kalomel Elektrode

a b

auch das Diffusionspotential bei *b* sich mit der Konzentration der variablen Lösung andert. (Die Kalomelelektroden waren bei diesen Versuchen mit 1/10 n NaCl-Lösung gefüllt.) Nach einer bekannten Formel kann für Verfünffachung der Konzentration die Anderung des Diffusionspotentials gleich $\frac{u-v}{u+v} \cdot 0.058 \cdot \lg 5$ gesetzt werden, diese Grösse kann für NaCl-Lösungen nicht so wie bei KCl vernachlässigt werden, da u und v nicht völlig gleich sind, es ergiebt sich vielmehr hierfür der Wert 0.008 Volt. Diese Anderung ist in dem Sinn, dass die variable Lösung mit steigender Verdünnung negativer gegen die Kalomelelektrode wird (da das negative Ion Cl eine grosser Wanderungsgeschwindigkeit als das positive Na hat). Somit ist die Anderung in dem gleichen Sinne wie die Gesamtwirkung der Konzentrationsänderung: bei Verdünnung wird die rechte Seite der obigen Kette positiver, und es ist von der gemessenen Gesamtdifferenz bei Verfünffachung der Konzentration 0.008 Volt abzuziehen, um die Differenz der b.P.D. zu erhalten.

Zur Berechnung möchte ich die zweite NaCl-Versuchsreihe, welche in der genannten Arbeit mitgeteilt ist, wählen, es war gefunden:

Konzentrations-Intervall	Differenz gefunden	Nach Abzug des Diff. Potentials	Berechnet
1/1250 bis 1/250	38	30	37.5
1/250 bis 1/50	36	28	37
1/50 bis 1/10	24	18	14.5

In einer anderen (nicht mitgeteilten) Versuchsreihe, für welche das Konzentrations-Intervall 1/50 bis 1/10 dieselbe Differenz der Kraft gab wie oben, ergab sich für

1/10 bis 1/2	13	5	3.5
1/2 bis 5/2	11	3	1.0

Für die Berechnung wurde in diesem Falle gesetzt

$$\log\frac{1}{\mathrm{m}}=\frac{0.052}{0.058}=0.8966$$

$$\mathrm{E}_{\mathrm{C2}}-\mathrm{E}_{\mathrm{C1}}=58\lg\frac{\mathrm{C}_2}{\mathrm{C}_1}-58\ \lg\frac{1+\sqrt{1+500^2\mathrm{m}^2\mathrm{C}_1{}^2}}{1-\sqrt{1+500^2\mathrm{m}^2\mathrm{C}^{12}}}$$

Die Uebereinstimmung mit den theoretischen Werten ist bei diesen letzten Versuchen weniger gut als bei den ersten. Ich glaube, das dadurch erklären zu können, dass diese letzten Versuchsreihen nicht an ein und demselben Objekt hintereinander durchgeführt wurden, somit von Unsicherheiten durch Verschiedenheit des biologischen Materials weniger frei sind. Die NaCl Versuche sind ausserdem mit den Unsicherheiten behaftet, die Berechnung von Diffusionspotentialen mit sich bringt.

Die hier abgeleiteten Formeln sind *nur bei binären Elektrolyten* gültig. Die Veränderlichkeit der b.P.D. gegen $CaCl_2$ oder $BaCl_2$, Lösungen worüber auch einige Versuche vorliegen, kann deshalb nicht in der gleichen Weise vorausberechnet werden. Die Theorie führt in diesem Falle auf Gleichungen dritten Grades, wodurch die mathematischen Ausdrücke alsbald eine sehr komplizierte Gestalt annehmen. Aus den vorliegenden Messungen scheint sich auch zu ergeben, dass der Gang der b.P.D. in diesem Falle etwas anders geartet ist, doch soll hierauf nicht näher eingegangen werden.

Zur richtigen Würdigung der vorliegenden Ergebnisse sei nochmals auf die Einzelannahmenhingewiesen, die zur Ableitung der Formeln nötig waren. Diese waren:

1. Gültigkeit des Verteilungssatzes (für Membran Lösung) in der einfachsten Form.

2. Ahnlichkeit der elektrolytischen Dissoziation in Membran und wässriger Lösung.

3. Unveränderlichkeit der Konzentration des Salzes KX (resp. NaX), welches den Elektrolyteigengehalt der Membran ausmacht von der äusseren wässrigen Konzentration. (d.h. vollständiger chemischer Umsatz in der Membran.)

Ohne diese Annahmen steigen die mathematischen Schwierigkeiten alsbald zum Unüberwundbaren, und es scheint mir dann eben unmöglich überhaupt zu quantitativen Beziehungen zu gelangen.

Man wird zugeben, dass diese Hilfsannahmenihrer Natur nach plausibel und in befriedigender Annäherung durch das Experiment bestätigt sind.

Ob und in wieweit sich bei Modification dieser Hilfsannahmen brauchbare Formeln ableiten lassen, soll späteren Untersuchungen vorbehalten werden.

BEZIEHUNGEN ZU NERNST'S THEORIE DER REIZUNG

In der früheren mehrfach erwähnten Arbeit, die der Verfasser mit Herrn Dr. J. Loeb ausgeführt, hat wurde bereits gezeigt, dass die Potentialdifferenzen an der Schnittfläche pflanzlicher Gewebe *qualitativ aber nicht quantitativ* sich ebenso verhalten wie solche an unverletzten Oberflächen: die Anderung der Potentialdifferenz mit der Konzentration der ableitenden Lösung erfolgt in demselben Sinne jedoch in erheblich kleinereren Beträgen. An der Hand der im Eingang dieser Arbeit gemachten Bemerkung, dass die Schnittfläche sich elektrisch wie ein Mosaik verhält, erscheint diese Beobachtung erklärlich. An der Grenze der durchschnittenen Membranteile wirkt die Konzentrations-Anderung wie an der unverletzten Rinde, an denjenigen Stellen jedoch, wo ableitende Lösung und Saft zusammenkommen, ist kein Einfluss der Konzentration auf die Potentialdifferenz vorhanden. Es sind also in diesen Versuchen gewissermassen zwei Ketten parallel geschaltet, solche mit wahren b.P.D. und solche mit Konzentrations-unabhängigen Diffusionspotentialen; der Gesammteffekt muss also offenbar eine kleinere Konzentrations-Veränderlichkeit als bei den b.P.D. sein, wie es auch tatsächlich beobachtet wird.

Möglich wäre es auch, die Erscheinungen an der Schnittfläche mit der Annahme zu deuten, dass die elektromotorisch wirksamen Membran mit einer fest anhaftenden wässrigen Phase bedeckt ist, die Konzentration der ableitenden Flüssigkeit kann sich dann nur durch Diffusion durch diese Schicht hindurch bemerkbar machen.

Tierische Gewebe der verschiedensten Art verhalten sich ähnlich den verletzten Pflanzenteilen, wie auch schon in der früheren Arbeit gezeigt wurde. Ich möchte an dieser Stelle noch einmal auf die interessanten Versuche von McDonald[1] und einen sich daraus ergebenden Zusammenhang mit der Nernst'schen Theorie der Reizung hinweisen.

---

[1] Proc. Roy. Soc. *67*, 310 (1900).

McDonald hat analoge Versuche mit Warmblüternerven ausgeführt, wie sie von Herrn Dr. Loeb und mir mit Pflanzenteilen beschrieben wurden. Freilich ist hiermit weder die von uns erreichte Pracision zu konstatieren, und es konnte deshalb auch nicht die hier gegebene physikalische Erklärung gewonnen werden. Die wässrige Lösung, die an der äusseren Oberfläche des Nerven haftet, wird durch Einlegen in Lösungen verschiedener Konzentration in ihrer Konzentration geändert, und damit die E.M.K., die man bei Ableiten von Oberfläche und Querschnitt misst (gewöhnlich als Verletzungsstrom bezeichnet). Bekanntlich ist die Oberfläche positiv gegen den Querschnitt, und sie wird um so positiver je verdünnter die Spüllösung ist, in welche der Nerv gelegt war und welche also an der Oberfläche haftet. Also selbst bei diesen Objekten wirkt die Konzentration in dem gleichen Sinn auf die b. P. D. Ist es hiernach nicht berechtigt, die Beziehung zwischen b. P. D., wie sie oben entwickelt wurde, als charakteristisch für Membranen verschiedenster Art Anzusehen, wenigstens in gewisser Annäherung?

Mit zahlreichen elektro-physiologischen Erscheinungen müssen die b. P. D. offenbar in Zusammenhang stehen. Besonders interessant scheinen mir die Beziehungen zu der Nernst'schen *Theorie der Reizung.* Die unter diesem Titel gewöhnlich zusammengefassten Gesetzmässigkeiten beruhen auf einem so soliden Fundament von Tatsachen, dass die Bezeichnung Theorie kaum sehr treffend ist. Nernst[1] hat gezeigt, dass die Erregung eines und desselben Muskels unter dem Einfluss von oszillatorischen oder alternierendem Stromfluss bei wechselnden elektrischen Bedingungen immer dann eintritt, wenn der Stromfluss (oder die Entladung) eine gewisse maximale Konzentrationsveränderung an Phasengrenzen zu Stande bringen kann. Die Konzentrationsänderung an der Phasengrenze zweier Elektrolyte ist hierbei denselben Gesetzmässigkeiten wie an einer Metall Elektrode unterworfen, z. B. als Funktion der Stromstärke und Wechselzahl eines Wechselstromes, als: const. $\frac{i}{\sqrt{m}}$, wo i die Stromstärke, m die Periodenzahl des Wechselstroms bedeutet. In der Tat zeigt sich, dass für alle Wechselströme, welche gerade die Reizung eines und desselben Nerv-Muskelpräperates hervorrufen können, dieser Quotient konstant ist. Wie wir gesehen haben, bedingen Konzentrationsänderungen Anderungen der Potentialdifferenz. Hiernach scheint es bei der Reizung auf eine gewisse *maximale Polarisation* an der Grenzfläche Membran Lösung anzukommen. Dass diese Polarisation durch Vermittlung einer damit verknüpften Anderung der Oberflächenspannung in die Kette der Vorgänge eingreifen kann, soll hier nur angedeutet werden. Bemerkenswert ist, dass der Electrolytgehalt der meisten Körperflüssigkeiten konstant 1/8 molekular ist. Ein Blick auf die Tabelle auf Seite 44 zeigt, dass diese Konzentration für die b. P. D. insofern eine besondere Bedeutung hat, als Konzentrationssteigerung *nur mehr eine sehr kleine Anderung hervorbringen kann, Konzentrationserniedrigung dagegen eine sehr viel grössere.* Dies scheint mir nach dem oben erklärten Zusammenhang zwischen Polarisation und Reizung mit der Tatsache verknüpft zu sein, dass gleiche Stromstösse in verschiedener Richtung sehr verschiedene Reizeffekte haben. Bekanntlich ist die Reizung bei Schliessung eines Stromes sehr viel stärker an der Katode als an der Anode, bei Offnung umgekehrt. Die Konzentrations-Verschiebungen in entgegengesetzten Richtungen bringen eben sehr verschiedene Anderungen der b. P. D. hervor. Ubrigens würde dies auch der Fall sein, wenn für die b. P. D. eine einfache logarithmetische Konzentrationsabhängigkeit bestände, da der Stromstoss, die Absolutwerte der Konzentration nicht ihr Verhältnis ändert. Bei Gültigkeit meiner Formel ist die einseitige Wirkung der Konzentrationsänderung jedoch noch besonders ausgeprägt, und am meisten für *die* Salzkonzentrationen, welche in den Körpersäften vorkommen.

---

[1] Proc. Roy. Soc. *67*, 310 (1900).

[2] Sitzungsber. d. preuss. Akad. 1908, I, 1. Siehe auch Pflüger's Archiv, 122, 307 (1908).

Eine andere Erscheinung, welche vielleicht in demselben Zusammenhange eine Erklärung ist, ist die folgende. Overton[3] erwähnt, dass die Reizbarkeit von Muskeln in hyperisotonischen Lösungen

---

[3] Pflüger's Archiv, *92*, 346.

(>1/8 mol) schneller verloren geht als in hypoisotonischen (<1/8 mol), obgleich in beiden Fällen schädigende Einflüsse sich bemerkbar machen. Die Tabelle auf Seite 44 zeigt, dass bei Konzentrationen, die wesentlich höher als 1/8 mol. sind, die b. P. D. sich nahezu in dem konzentrationsunabhängigen Gebiete befindet, es ist keine Polarisation möglich und damit der Erregungsvorgang gehemmt. Es soll indes nicht geleugnet werden, dass Konzentrationsänderung in diesen Fällen auch durch osmotische oder chemische Vorgänge Veränderungen im Gewebe hervorrufen kann, die ihrerseits die Reizbarkeit beeinflussen.

Höber nennt in seinem Buche ueber die physikalische Chemie der Zellen die konstante Körpertemperatur und den konstanten Salzgehalt des Blutes als die zwei auffallendsten allgemeinen Eigenschaften aller höheren Organismen. Für die Bedeutung der erhöhten Temperatur lässt sich eine Erklärung, wie er zeigt, geben, nicht aber für den konstanten Salzgehalt. Eine solche ist hier gelungen, meines Wissens zum ersten Male.

CONCLUSIONS

1. Potential differences at the junction of an uninjured part of a plant and an aqueous solution of an electrolyte vary with the concentration of the electrolyte, as Dr. Loeb and the writer have shown.

2. The following formula was derived representing the relation between variation of potential difference and concentration.

Pot. Diff. 1 — Pot. Diff. 2

$$=0.058 \log. \frac{C_1}{C_2} - 0.058 \log \frac{1+\sqrt{1+10^6 m^2 C_1^2}}{1+\sqrt{1+10^6 m^2 C_2}}$$

where is given by the relation

$$\log. \frac{1}{m} = \frac{\text{limit of the pot. diff.} - \text{pot. diff. for } c = n/500}{0.058}$$

In the derivation of this formula the following assumptions were made: (a) that a complete reaction takes place between a constituent of the membrane and the aqueous electrolyte. In this reaction a salt is formed which is insoluble in water but distributed in the membrane homogeneously. (b) that the electrolyte as such is contained in the membrane in minimal concentration and that

in accordance with the law of partition the ratio of concentration of electrolyte in membrane and in water is constant.

3. The formula was tested experimentally by means of measurements on apples (table, page 44). As required by the formula at high concentrations the difference of potential approaches a limit; at low concentrations the potential difference follows a simple logarithmic relation; the formula is also valid for intermediate concentrations.

4. If we assume that variations in potential difference induce stimulation, it is possible from the results given above *and* with aid of *Nernst's theory of stimulation* to explain some electrophysiological observations; examples of which are (1) the different effect on stimulation of cathodical closing and of anodical closing; (2) the diminution of irritability in hypertonic salt solutions.

THE PRESENT STATUS OF THE TEMPERATURE SCALE

By George K. Burgess, Sc.D.
Bureau of Standards, Washington, U. S. A.

The past few years have been marked by great advances in the exact determination of the temperature scale in terms of fixed points of melting, transformation, or boiling, of pure substances, extension of the scale both upwards and downwards, the correlation of the various physical phenomena and their mathematical expression in terms of which interpolations and extrapolations may be expressed, and in the invention and improvement of temperature measuring apparatus and methods.

The Thermodynamic Scale. The fundamental basis for the determination of the temperature scale is obtained by measurements with some form of gas thermometer. The accuracy with which these and auxiliary measurements may now be made, together with the great purity now obtainable of the materials suitable for standard points, and the state of our knowledge of the gas laws, permits the expression of temperatures in terms of the *thermodynamic* or ideal-gas scale, a scale which is independent of the properties of any particular substance and to which the usual gas scales approximate so closely that, for most purposes, it is not necessary to distinguish between them. The radiation laws, in terms of which extrapolation to the highest temperatures is made, are also based on the thermodynamic scale; so that, using this as our standard, we have a single temperature scale from the lowest to the highest temperatures. The corrections to apply to the scales given by gases, to reduce to the thermodynamic scale, are not yet known with all the certainty that may be desired especially at very low and very high temperatures, but in the former region the thermometric gases used, hydrogen and helium, depart less from the ideal state than any others, and in the case of helium the correction is practically negligible over almost the complete range of temperatures.

In the most recent researches in exact gas thermometery it is more and more the practice to reduce results to the thermodynamic scale, a practice that should become universal.

The Gas Scales. The only methods of temperature measurement that are directly reducible to the thermodynamic scale are those based on the gas thermometers at constant pressure and constant volume, by means of computations based on the known properties of these gases.

The following table (Table I) based on recent computations[1] represents well enough the corrections to the gas scales in ordinary use and over the ranges within which these gases may be used to advantage.

TABLE I. SCALE CORRECTIONS FOR GASES. θ_0=273°.10 C.

Temperature Centigrade	Constant Pressure=76 cm.			Constant Volume, p_0=100 cm.		
	Helium	Hydrogen	Nitrogen	Helium	Hydrogen	Nitrogen
−250	......	......	......	+.02	......	......
−200	+.10	+.26	......	+.01	+.06	......
−100	+.03	+.03	+.33	.000	+.014	+.07
−50	+.009	+.004	+.09	.000	+.004	+.02
+25	−.002	−.002	−.013	.000	.000	−.006
+50	−.002	−.003	−.017	.000	.000	−.006
+75	−.002	−.002	−.012	.000	.000	−.004
+150	+.005	+.003	+.04	.000	+.001	+.01
+200	+.01	+.01	+.10	.000	+.002	+.04
+450	+.07	+.04	+.50	.00	+.01	+.15
+1000	+.24	+.01	+1.7	......	+.04	+.70
+1500	......	......	+3.0	......	......	+1.3

Within the fundamental interval, 0° to 100° C., the temperature scale has been defined by the International Committee on Weights and Measures in terms of hydrogen at constant volume under a pressure of 1000 mm. of mercury. This scale, as closely as it is known, appears to be practically identical with the thermodynamic scale. For lower temperatures the hydrogen and helium scales are used, the latter for the very lowest attainable, or to less than 1°2 K according to Kammerlingh Onnes. For high temperatures, especially above 450° C., nitrogen at constant pressure is usually used although there is not here, nor for the range below 0° C., any international agreement as to the temperature scale. The upper limit attained is the melting point of palladium, 1550° C. There is no necessity, at least from the point of view of the determination of temperatures, of extending gas thermometer measurements higher than this, as the thermodynamic scale is more nearly realized for those high regions by means of instruments based on the radiation laws the constants of which may be determined below 1550° C.

---

[1] See in particular computations by:
Callendar, Phil. Mag. (6) *5*, 48, 1903.
D. Berthelot, Trav. et Mém. Bur. Int. *13*, 1903.
Buckingham, Bull. Bureau Standards *3*, 237, 1907.
Kammerlingh Onnes and Braak, Seiden Coms. 97b, 102b, 1907.
Rose Innes, Phil. Mag. (6) *2*, 130, 1901.

Secondary Methods and Scales. The most commonly used secondary temperature measuring instrument is the *mercury in glass thermometer*, the reductions of which to the hydrogen or thermodynamic scale, after all other corrections are made, depends on the kind of glass of which it is made and to a much smaller extent on the history of the thermometer. The normal hydrogen scale is preserved at the International Bureau by means of four *verre dur* thermometers.

For high temperature thermometers — from 300° to 520° C. or more — the mercury is confined under pressure exerted by an inert gas; and if quartz is substituted for glass, 750° C. may be reached with mercury. For low temperatures the mercury may be replaced by toluene to $-90°$, and by pentane to liquid air temperatures.

All thermometers of the above types have to be calibrated empirically and individually in terms of known standards of temperature.

The Platinum Resistance Thermometer over the range in which it remains constant and sensitive, from $-200°$ C. to $+1000°$ C., and when properly designed, constructed and used, is the most exact secondary instrument we have, and has been of great service recently in coördinating and comparing the gas thermometer observations on basal temperatures of several recent observers.[1] For example, the lower freezing-point values, cadmium, zinc, etc., of Day and Sosman,[1] as well as boiling points of naphthalene and benzophenone by Jaquerod and Wassmer,[2] were shown definitely by the resistance thermometer measurements of Waidner and Burgess[3] to be incompatible with the most probable value of the sulphur boiling point (=S.B.P.), one of the most important of the base points, as it is commonly used with the freezing and boiling points of water, as the third calibration point of platinum resistance thermometers. The latest work on the sulphur boiling point[4] with the constant volume gas thermometer has reduced the uncertainty of this temperature, which we may take as 444.6 on the thermodynamic scale, to less than 0°.1 C., whereas a year ago this uncertainty was nearly 1°.0 C.

---

[1] Holborn and Henning, Ann. d. Phys. *35*, 761, 1911.
Waidner and Burgess, Bull. Bureau Standards *6*, 149, 1910; *7*, 1, 1910.
Dickinson and Mueller, Jl. Wash. Acad. Sci. *2*, 176, 1912.

The usual Callendar, or difference formula for reducing platinum temperatures, $pt=100\ (R-R^0)\ /(R^{100}-R^0)$, to true temperatures, namely: $t-pt=\delta(t/100-1)\ t/100$, where δ is a function of the purity of the platinum, has been shown recently[5] to be of more general and exact application over a wider range of temperature than had hitherto been supposed. Using a base point within the fundamental interval such as the transformation point of sodium sulphate, 32°.383[6] as the third calibration temperature, the value of δ for pure platinum is 1.47_0 to 1.48_0, and using the S.B.P., 444.6, the value of δ is 1.48_4 to 1.49_4. In other words, calibrating a platinum resistance thermometer in ice, steam and sulphur vapor will give the normal International Hydrogen Scale, within the fundamental interval, 0° to 100°, to 0.004° C. or to closer than the International Bureau can reproduce its scale with certainty. In this range the platinum thermometer is reliable to better than 0°.001 C. Using the platinum thermometer at high temperatures,

[1] Day and Sosman, Am. Jl. Sci. *29*, 93, 1910. Reprint 157, Carnegie Institution of Washington, 1911.

[2] Jaquerod and Wassmer, Jl. Chim. Phys. *2*, 52, 1904.

[3] Waidner and Burgess, l. c.

[4] Holborn and Henning, l. c.
Day and Sosman, Am. Jl. Sci. *33*, 517, 1912. Jl. Wash. Acad. Sci. *2*, 167, 1912.

[5] Adams and Johnston, Am. Jl. Sci. *33*, 534, 1912. Jl. Wash. Acad. Sci. *2*, 275, 1912.
Holborn and Henning, l. c.
Dickinson and Mueller, l. c.
Waidner and Burgess, l. c.

[6] Richards and Wells, Zs. Phys. Chem. *43*, 465, 1903.
Dickinson and Mueller, Bull. Bureau Standards, *3*, 641, 1907.

or to 1100° C., in the same way with the Callendar formula, the temperature scale is reproduced as closely as this scale has been located by gas thermometer measurements, or to within 2° at 1100° C. It has been suggested to write the δ in the form $\delta = \delta + a\,t$. There appears to be no certain advantage of this more complex expression, however, for pure platinum.

For very low temperatures the Callendar formula breaks down, but to −200° C. it may be used with considerable exactness if the boiling point of oxygen −182.9, or the sublimation point of carbonic acid, −78°.34, is taken as the third calibration temperature. Complex exponential functions have also been suggested for very low temperatures, and resistances expressed in powers of temperature even to the fifth are sometimes used.

In precision calorimetry, the platinum thermometer replaces that of mercury to advantage, for when properly constructed the former has no appreciable zero change or hysterisis with use and time if not exposed to high temperatures, and it is as easy to measure small temperature differences at 25° C. to 0°.0001 C. with the platinum as to 0°.001 with the mercury thermometer. A great and unique practical advantage of the former for all uses above −100° C. is the fact that its calibration is made and controlled by only three fixed points which are easily realized with exactness, two of which are the ice and steam points and the third *any* other known temperature which is most convenient.

The platinum thermometer becomes, therefore, the most satisfactory secondary standard for the calibration of all other types of thermometers between −200 and +1100° C. In fact, if the International Bureau were destroyed and all the existing copies of its thermometer standards as well, the International scale would be perpetuated with entire satisfaction by means of the platinum thermometer which may be constructed and calibrated independently anywhere it may be desired.

The Thermoelectric Thermometer, in general, is not an instrument of such great precision nor of such simple calibration as the platinum resistance thermometer, a formula involving three and even four or more powers of temperature in terms of E.M.F. being required for all thermocouples used with the highest accuracy over several hundred degrees and at low temperatures over very much shorter ranges.[1]

For temperatures below −200° C. a thermocouple of gold-silver[2] appears to best meet the requirements of a secondary instrument. For ordinary temperatures satisfactory couples are those of iron-constantan and copper-constantan; for high temperatures the LeChatelier couple of Pt, 90 Pt-10 Rh.

For a moderate precision, the thermocouple is a most convenient instrument and the calibration may then be reduced to three or even two reference temperatures. In the last case, for the Pt-Rh couple, the best formula appears to be Holman's, $\log e = a + b \log t$, for which, if the zinc and copper freezing points are used as calibrating temperatures, the scale is off by less than 2°.5 between 200 and 1300° C. and by less than 5° to the melting point of platinum. For no form of thermocouple does it appear that the inverse function, which is the more convenient to work with, namely, $t = a + be + c\,e^2 + d\,e^3 + \dots$, represents the temperature scale with the same exactness as the form $e = a + bt + ct^2 + dt^3 + \dots$ with a like number of terms.

In the following table (Table II) are given the corrections to the readings of Pt, 90 Pt-10 Rh thermocouples calibrated at the freezing points of zinc, antimony and copper (see Table III) for the usual three-term formula and in zinc and copper for the formula of two terms. The couples of Pt, 90 Pt-10 Ir have nearly the same corrections.

TABLE II. CORRECTIONS TO THERMOCOUPLE SCALES
(PT, 90 PT-10 RH.)

Formula t=	300	600	900	1200	1400	1600	1700	1750
$e = a + bt + ct^2$	−0.8	0	+0.3	+0.5	+8	+26	+40	+46
$\log e = a + bt$	−0.6	+1.5	+2.5	−5	−5	−3	+1	+3

---

[1] Day and Sosman, l. c., and Sosman, Am. Jl. Sci. *30*, 1, 1910. Platinum rhodium at high temperatures.

Dickinson, Mueller and White: Copper constantan between 0−100. Phys. Rev. *31*, 159, 1910.

Adams and Johnston: Cu—Cn between 0 and 300, l. c.

J. Clay: Couples at very low temperatures. Leiden Coms. 107d, 1908.

[2] J. Clay, l. c.

The inherent weakness, as compared with the platinum resistance thermometer, of any thermocouple as a secondary temperature standard is the impossibility of eliminating in the measurements the E.M.F. effects along the whole length of the wires between hot and cold junctions of the thermocouple, and no wire yet examined appears to be completely free from such effects of inhomogeneity.

For the estimation of very high temperatures we have the *radiation laws of Wien and of Stefan,* preference being given to the former based on the use of monochromatic light, mainly on account of experimental convenience, although the theoretical foundation of the second based on the use of total radiation is the more certain. The characteristic constants of neither of these laws are as yet determined in a wholly satisfactory manner, although considerable has been done in recent years on this subject, and work is still in progress.

We may take the value 14,500 for the characteristic constant c_2 in Wien's law $\log I/I_1 = c_2 \lambda \log e \ (1/T_1 - I/T,)$ in which I is the intensity of light of wave-length λ at an absolute temperature T. The recent determinations of c_2 all lie between 14,200 and 14,600. For the constant σ of Stefan's law connecting total radiation and temperature, $E = \sigma \ (T^4 - T_o^4)$, the value $\sigma = 5.80$ watt. cm.$^{-2}$ deg.$^{-4}$ appears to be the most probable, although the range of recent determinations is 5.30 to 6.51.

Standard Temperatures. Limiting ourselves to determinations made since the year 1900, and selecting only temperatures in the location of which two or more independent observers have participated, and which are suitable to use as check points in physical and chemical operations, the following temperatures (Table III) may be used as standard. They are given in terms of the thermodynamic scale, and for above 1550° C., the constant c_2 of Wien's law is taken as 14,500. Boiling points are for a pressure of 760 mm. Hg, and are given only for substances that do not attack platinum and for which it has been shown they remain constant over long periods of boiling.

TABLE III. STANDARD TEMPERATURES. THERMODYNAMIC SCALE

Substance	Phenomenon	Temperature C	Uncertainty C°	Repr'ducibility C°
Hydrogen	Boiling	−252.7	0.2	0.05
Oxygen	Boiling	−182.9	0.1	0.03
Carbon dioxide	Sublimation in gasolene	−78.34	0.1	0.03
Mercury	Freezing	−37.7	0.1	0.05
Water	Freezing	0	0	0.001
$Na_2SO_4+10H_2O$	Transformation to anhydrous salt	32.383	0.002	0.001
Water	Boiling	100	0	
Naphthalene	Boiling	271.96	0.02	0.01
Tin	Freezing	231.85	0.1	0.05
Benzophenone	Boiling	305.90	0.05	0.02
Cadmium	Freezing	320.92	0.1	0.03
Lead	Freezing	327.4	0.1	0.05
Zinc	Freezing	491.4	0.1	0.15
Sulphur	Boiling	444.6	0.1	0.03
Antimony	Freezing	630.	0.5	0.3
Ag_3-Cu_2	Eutectic freezing	779	1.0	1.0
NaCl	Freezing	800	2.0	1.0
Silver	Freezing	960.5	1.0	0.5
Gold	Freezing	1063	2.0	1.0
Copper	Freezing	1083	2.0	1.0
Palladium	Freezing	1549	10	3
Platinum	Melting	1755	15	5
Alumina	Melting	2000	30	20
Tungsten	Melting	3000	100	25
Carbon arc	Pos. crater	3600	150	50
Sun	Surface	6000	500	100

For the temperatures dependent on atmospheric pressures we have:

Oxygen B.P. $T=T_{760}+0.013\ (p-760)$
Carbon dioxide S.P. $T=T_{760}+0.017\ (p-760)$
Water B.P. $T=T_{760}+0.037\ (p-760)$
Napthalene B.P. $T=T_{760}+0.058\ (p-760)$
BenzophenoneB.P. $T=T_{760}+0.063\ (p-760)$
Sulphur B.P. $T=T_{760}+0.0912\ (p-760)-0.000042\ (p-760)^2$

As to the chemical purity of the various substances, Mylius has shown[1] that the following metals may easily be had to 0.01 per cent or better: Au, Ag, Pt, Hg, Cu, Sn, Pb, Cd, Zn. Of the boiling substances, benzophenone and oxygen are the only ones to the purity of which special attention need be given. Due perhaps to the general practice of investigators working at very low temperatures to use the gas thermometer itself, instead of an auxiliary method, for measuring those temperatures, there is a dearth of exactly known fixed points in this part of the scale.

---

[1] F. Mylius, Zs. Anorg. Ch. *74*, 407, 1912.

Examples of Standard Temperatures. Some of the standard temperatures, owing to their great importance, have been determined many times and are therefore particularly valuable as primary reference points. The actual status of our knowledge of the temperature scale is perhaps best illustrated by giving in detail the measurements since 1900 on some of the most carefully studied of these temperatures, such as the boiling points of oxygen and sulphur and the melting points of cadmium, gold, platinum, and tungsten.

OXYGEN BOILING POINT = *−182.9*

DATE	OBSERVER	METHOD	TEMPERATURE	
			Observed	Thermo-dynamic
1901	Holborn	H_2 scale const. vol.	+182.7	
1901	Dewar	H_2 scale const. vol.	−182.5	
1906	Grummach	Pentane therm.	-182.6_6	
1906	Travers, Jaquerod and Senter	H_2 scale const. vol. He scale const. vol.	-182.9_3 −182.8	-182.8_7
1908	Kammerlingh Onnes and Braak	H_2 scale const. vol.	-183.0_4	-182.9_9

SULPHUR BOILING POINT = *444.6*

1902	Chappuis and Harker	N_2 scale const. vol.	444.7[1]	444.8
1908	Eumorfopoulos	Air scale, const. press.	444.5_5[2]	444.9_3
1911	Holborn and Henning	H_2, He const. vol. N const. vol.	444.5_1[1] 444.3_9	444.5_1
1912	Day and Sosman	N_2 scale const. vol.	444.4_6[2]	444.5_5
1912	Dickinson and Mueller	(Day and Sosman's therm.)	444.2_8[1]	444.3^8

[1] Transferred by platinum resistance thermometer.

[2] Thermometer bulb in S vapor.

CADMIUM MELTING POINT=*320.9_2*

DATE	OBSERVER	METHOD	TEMPERATURE	
			Observed	Thermody'mic
1900	Holborn and Day	N_2 scale const. vol.[1]	321.7	321.8
1902	Kurnakow and Puschin	Thermocouple interpolation	321.0	
1904	Day and Allen	Thermocouple interpolation	321.7	
1909	Waidner and Burgess	Pt. resis. (S.B.P. =444.60)[2]	320.9_4	320.9_4
1910	Day and Sosman	Thermocouple extrapolation[1]	320.0	320.1
1911	Holborn and Henning	H_2, He, N_2 scales const. vol.[2]	320.9_2	320.9_2
1912	Day and Sosman	Corrected from 1910 value[1]	320.8	320.9
1912	Adams and Johnston	Cu-Cn thermocouple interpolation	320.9_2	320.9_2

GOLD MELTING POINT[3]=*1063*[4]

1900	Holborn and Day	N_2 scale const. vol.	1064.0	1064.3
1902	D. Berthelot	Air-optical const. press.	1064	1065.6
1904	Jaquerod and Perrot	Air,CO,N_2,O_2 const. vol.	1067.2	1067.4
1908	Day and Clement	N_2 scale const. vol.	1059.3[5]	1059.5
1910	Day and Sosman	N_2 scale const. vol.	1062.4	1062.6

PLATINUM MELTING POINT=*1755* (BASIS: C_2=14,500)

Date	Authors	Method	Temperature
1903	Nernst	Total light from black body	1782
1905	Holborn and Henning	Combined optical and thermoelectric	1729
1905	Harker	Thermoelectric	1710
1906	Nernst and Wartenberg	Optical: Wien's law	1753
1907	Holborn and Valentiner	Optical: Wien's law	1760
1907	Waidner and Burgess	Optical: Wien's law	1753
		Radiation from Pt, 3 colors	1750
		Therm'lectric: various formulæ	1697–1757
1909	Féry	Radiation from Pt oxidizing at	1690
		Radiation from Pt reducing at	1740
1910	Sosman	Thermoelectric extrap. from Pd = 1549	1752
1910	Ruff	Optical about	1750

---

[1] Transferred by Pt-Rh thermocouples.

[2] Transferred by platinum resistance thermometer.

[3] All measurements were made by transfer with Pt-Rh thermocouples.

[4] Several determinations of the copper melting point (1083) have also been made and auxiliary methods have shown Cu − Au = 20° so that the gold point is better known than the table would indicate.

[5] Sample shown to contain iron from crucible.

TUNGSTEN MELTING POINT$=\mathit{3000}$ (BASIS: $C_2=14{,}500$)

1906	Waidner and Burgess	Wien's law, lamp filament	32.00
1907-10	Waidner and Burgess	Wien's law, lamp filament	3080–3050
1907	Wartenberg	Wien's law, Wenhelt discharge	2930
1910	Pirani	Wien's law, lamp filament	3226
1910	Ruff and Goecke	Wien's law, in vacuum furnace	2597
1911	Forsythe	Wien's law, with wedge with vacuum furnace	2974 3030
1911	Pirani and Meyer	Wien's law with filament and strip	2997
1911	Langmuir	Total photometric	3177

International Temperatures. It is evidently of the greatest importance for chemists and others who have to express or locate many of their results in terms of temperatures, that they be able to do so in terms of a common scale, as otherwise confusion reigns when endeavoring to compare the numerical values assigned by different observers to the various phenomena.

For the past twenty-five years, thanks to the International Bureau of Weights and Measures, it has been possible to express results to 0°.002 C. within the fundamental interval 0° to 100° C., but outside this interval chaos has reigned.

Both at low temperatures and high, there have been almost as many scales as observers, and some of the outstanding differences were relatively very large, even within the past year, for example, 1° at the sulphur boiling point and 7° at the gold melting point.

The recent series of investigations mentioned above have rendered it possible, however, to greatly reduce the uncertainties, and the state of the art of temperature measurements is now such that it should not be difficult for the various standardizing laboratories to agree upon a common temperature scale which would be defined in some such manner as outlined above. In pursuance of this idea, the several national laboratories and the International Bureau are at present interchanging communications relative to the establishment by agreement of some such single temperature scale, and it is to be hoped that the outcome of these interchanges will be of great practical benefit and convenience for the certification and use of temperature-measuring instruments, and that thenceforth 500° C. or 1000° C., for example, will each convey but one idea of temperature as do 0° or 100° C. at the present time.

SUR LES THEORIES ET LES FORMULES DE LA CHIMIE-PHYSIQUE

PAR M. ALBERT COLSON
Professeur à l'Ecole Polytechnique, Paris, France

1.—*Les Théories*

A coté de l'admirable loi des phases de Gibbs,[1] la Chimie-Physique présente un ensemble de résultats véritablement illusoires. Déja, en 1901, M. Kahlenberg[2] et ses élèves, par des expériences précises et nombreuses, ont prouvé que la théorie de la dissociation électrolytique n'explique pas les phénomènes présentés par les solutions aqueuses.

En 1904, ayant étudié ces questions dans le but de vérifier des résultats suggérés par les expériences de Blondlot sur les rayons N, je suis arrivé aux mêmes conclusions que M. Kahlenberg,[3] et j'aimontré:

1o. Que l'action des bases dissoutes K.OH ou $Ba(OH)^2$ sur les sulfates métalliques est différente suivant que l'onver se la base dans le sel dissous, ou le sel dans la base;

2o. Que le pouvoir cryoscopique moléculaire des sulfates chromiques est en rapport avec l'hydrolyse de ces sels, mais qu'il est indépendant de leur degré d'ionisation.

Sans doute, l'hydrolyse ne suffit pas à expliquer les phénomènes de dissolution, et M. Arrhénius a été très bien inspiré en affirmant la nécessité d'un autre dédoublement de la particule dissoute. De l'hypothèse de Van't Hoff, touchant l'état moléculaire de la particule dissoute, M. Arrhénius a déduit le dédoublement en ions des sels et des acides minéraux dissous. Il confirmait ainsi l'idée de Williamson et de Clausius que la conductibilité des solutions nécessite la préexistence des ions dans les solutions conductrices. L'hypothèse Willamson-Clausius qui a donné un si grand poids à l'interprétation de M. Arrhénius, ne s'accorde peut être pas aussi bien avec les faits que celle de Sir Ol. Lodge. D'après ce savant, la séparation en ions ne préexiste pas; elle ne se fait qu'au moment du passage du courant.

---

[1] Bancroft. Che Phase rule.

[2] L. Kahlenberg. The Theory of electrolytic dissociation,Bul. of the Univers. of Wisconsin, fev. 1901. Physic-Chemistry, 1901.

[3] C'est l'occasion de rappeler que ce grand savant a maintefois photographié les phénomènes d'extinction qu'il a signalés, et qu'il n'a jamais approuvé les exágérations publiées sur ce sujet, dont on n'est pas encore maitre des causes.

Dans la première hypothèse, la conductibilité d'une solution saline, déterminée par le nombre des ions préexistants, serait invariable à température fixe. Dans l'hypothèse de Sir Ol. Lodge, il se pourrait que des perturbations dans la conductibilité des sels, se fissent sous l'action du courant quand plusieurs modes d'ionisation sont possibles.

Voici quelques expériences qui me paraissent confirmer cette opinion. Elles sont relatives à la résistivité d'une solution de sulfate chromique violet à 2/10 Molécule par litre (Analyse: $Cr^2O^3=0{,}315$, $SO^4Ba=1{,}417$). La détermination à 0°, de la résistance X de la solution par rapport à une résistance totale R à été obtenue à l'aide de l'appareil téléphonique de Dongier-Lesage, par l'équation suivante:

$$\frac{X}{R}=\frac{a}{1000-a}$$

dans la quelle a représente la longueur de lar ègle qui correspond à l'extinction du téléphone. Généralement la valeur de a se détermine très nettement et très exactement.[1]

Cependant, dans les solutions chromiques qui nous occupent, varie à la longue. Voici les nombres observés de minute en minute à 0°, sur une solution de 24 heures:

$R=23{,}08$ $a=384$; 386; 387; 387;

$R=13{,}08$ $a=525$; 526; 527; 529; 530.

Une solution à 1/10 Molécule par litre donne:

$R=23{,}08$ $a=506$; 509; 510; 510.

La même solution abandonnée pendant 48 heures à la température ambiante, s'hydrolyse légèrement et donne à 0:

$R=23{,}08$ $a=488$; 498; 501; 504; 506; 507.

Il semble qu'avec le temps, on retrouve le nombre précédent 510. Mais si on laisse circuler le courant, la valeur a retombe à

---

[1] Bull. de la Soc. Chim. 1908 et 1911, T. 9, p. 576 et 862.

501 au bout d'une minute, à 499 au bout de deux minutes, à 497 au bout de trois minutes.

Si de nouveau, on arrête le courant, on observe
ave R = 23,08, au bout de 2 minutes: $a = 504$,
au bout de 3 minutes: $a = 506$,
au bout de 7 minutes: $a = 509$,
au bout de 12 minutes: $a = 511$.

Le courant ayant été rétabli pendant une minute, on retombe à 505,5 et à 505 au bout de 2 minutes.

Après une nouvelle suppression de courant pendant 2 minutes on trouve: $a = 512$,
après suppression pendant 4 minutes, on trouve $a = 515$,
après suppression pendant 6 minutes, on trouve $a = 516$,
après suppression pendant 7 minutes, on trouve $a = 516$.

Un nouveau passage de courant pendant 1 minute redonne 507, puis 505 après 2 minutes. La valeur de a s'est élevée de 488 à 516.

La même liqueur deux fois plus étendue (c'est-à-dire au 1/100 Molécule) donne à 0° et de minute en minute:

Pour R = 93,08, $a = 596$; 597; 598; 600; 602.

Si on fait circuler le courant pendant 1 minute, on retombe à 599; si on l'arrète, on remonte à 602.

Les sulfates verts donnent des résultats analogues mais moins marqués.

On pourrait supposer que le passage prolongé du courant détermine un échauffement et diminue la résistance de la solution placée dans la glace. Je ne le crois cependant pas, car je n'ai rien constaté de semblable sur d'autres corps. En tout cas, chaque fois que la liqueur a été soumise à l'influence du courant, la conductibilité du sel refroidi change: a passant de 498 à 504 puis à 512.

Le courant parait donc agir sur le degré d'ionisation, loin d'être toujours réglé par cette condition. De sorte que la nécessité d'une ionisation préalable, indispensable au passage du courant, n'est plus une objection aux conclusions de M. Kahlenberg remémorées ci-dessus.

Déjà dans l'eau, M. Kahlenberg a signalé des molécules non dissociées qui sont conductrices. J'ai ensuite prouvé que la conductibilité des sulfates chromiques isomères n'a aucune relation avec leur degré d'ionisation. Dans certains solvants organiques, M. Kahlenberg et MM. Jones, Castoro....ont montré que la molécule reste normale et que néanmoins la conductibilité existe. MM. Walden, Werner, Lincoln, Dutoit....ont étendu ces observations à une dixaine de solvants.

Il résulte de ces faits que la conductibilité par ionisation des sels métalliques étant exceptionnelle, ne doit pas être érigée en règle.

L'HYPOTHESE DE VAN'T HOFF ET LA THERMODYNAMIQUE

Pour ces motifs et pour d'autres que je ne puis rappeler ici, puisque le Règlement du Congès s'y oppose, j'estime que le fondément de la Théorie des Ions, c'est-à-dire l'hypothèse de Van't Hoff elle même, est illusoire.

Discutons directement l'assimilation de la particule dissoute à la molécule gazeuse. Le fondement que lui a donné Van't Hoff n'a qu'une apparence de solidité. Il repose uniquement sur ce que la pression osmotique moléculaire π serait voisine de la pression moléculaire P qu'aurait le sucre s'il existait à l'état gazeux à la température ordinaire. De ce fait, il est en effet facile de conclure que $\pi. V=RT$ puisque $P.V$ est égal à RT. Van't Hoff a préféré calculer R et conclure de $\pi V=RT$ l'égalité $\pi=P$.

1o. D'une part, il n'est pas certain que la molécule gazeuse du sucre soit $C^{12}H^{22}O^{11}=342$, à basse température. Autant admettre que la molécule du soufre est S^2 par analogie avec l'oxygène O^2.

Sans doute, si les expériences de Pfeffer, différant de 508 à 554, pour une même concentration, étaient peu faites pour admettre l'égalité $\pi=P$, celles de MM. Morse et Frazer ont donné depuis de milleurs résultats. Néanmoins, pour conclure que $R=847$, il ne suffit pas que la loi de Mariotte soit applicable, il faut encore que le coefficient de Gay-Lussac $\alpha=0{,}00366$, s'applique identiquement aux particules dissoutes et aux gaz. Or cette condition est douteuse d'après Ponsot, et d'après Lord Berkeley et M. Harteley. Aux fortes pressions surtout, la dilatation de la particule dissoute est à peine sensible même entre 4 et 24, tandis que, pour la molécule d'une vapeur comprimée, le coefficient α est supérieur à 0,00366.

Enfin, les expériences de M. Fouard (Journ. de Phys. 1911), montrent qu'avec des membranes en fulmicoton, les tensions osmotiques moléculaires changent, tout en restant à peu près égales entre elles, avec cette membrane particulière.

L'osmose semble donc être une fonction des membranes.

2o. D'autre part, les comparaisons isotoniques n'ont jamais été faites sur des mesures osmotiques, mais sur des déterminations cryoscopiques ou tonométriques.

L'identification de ces mesures reposant sur un cycle thermodynamique, a été considérée comme irréfutable. Pourtant, la légitimité de ce cycle est douteuse aux yeux de nombreux savants compétents. De fait, les résultats osmométriques ne sont aucunement comparables aux déterminations de Raoult. En effet, l'équation $\pi.V=RT$, fondement de l'osmométrie, indique que les comparaisons sont d'autant plus rigoureuses que les solutions sont plus diluées (moins concentrées, comme pour les gaz). Cette loi limite ne convient au contraire ni à la tonométrie, ni à la cryoscopie, où les solutions favorables dépassent parfois la concentration de 10%, et où les solutions diluées d'éloignent de plus en plus de la valeur théorique indiquée par la formule théorique:

$$K.M=0{,}02\frac{T^2}{L}$$

Cette formule donne aux Chimistes une impression de rigueur devant laquelle ils s'inclinent, et la valeur du poids moléculaire M qu'elle relie exclusivement à la température de fusion ou d'ébullition T du solvant et la chaleur latente correspondante L, apparait à leurs yeux, comme une détermination absolue et indépendante de toute hypothèse. Ils oublient que K est un coefficient spécifique cèlatif au corps dissout et que 0,02 est le quotient, par l'équivalent mécanique 425, du nombre R supposé égal à 847, pour la particule dissoute comme pour la particule gazruse.

En réalité, la formule $K.M=0{,}02\,\frac{T^2}{L}$ ne se relie à la thermodynamique que par un emprunt à l'équation de Clapeyron et elle n'est plausible que sous certaines conditions expérimentales que nous allons analyser.

Soient f et f' les tensions de vapeur du solvant et de la dissolution, *n* le nombre de molécules contenues dans le poids P de la substance dissoute dont la poids moléculaire est M, d'où $n=\frac{P}{M}$; Raoult a exprimé sa loi (*Scientia.– Tonométrie,* p. 43) par l'expression

$$\frac{f-f'}{nf}=A, \text{ ou } \frac{df}{f}=A\frac{P}{M} \quad (I)$$

La diminution moléculaire de tension A est constante quelle que soit la substance dissoute.

Si l'on admet qu'en solutions étendues, l'équation de Clapeyron s'applique au solvant dont on néglige le volume liquide, on aura:

$$L=\frac{T}{42f}\ u\ \frac{df}{dT}$$

D'autre part, pour une molécule de vapeur normale:

$$uf=RT \text{ d'où: } L=\frac{T}{425}\times\frac{RT}{f}\times\frac{df}{dT}=\frac{R}{425}\times\frac{T^2}{f}\times\frac{df}{dT} \quad (II)$$

Comme: $\frac{R}{6y}=\frac{84f}{42f}$, c'est-à-dire sensiblement 2, si dans l'égalité II, nous remplaçons $\frac{df}{f}$ par sa valeur tirée de l'équation I, nous aurons:

$$L=2\frac{T^2}{dT}\times\frac{AP}{M} \quad \text{ou:} \quad M\frac{dT}{P}=2A\times\frac{T^2}{L}$$

Le coefficient $\frac{dT}{P}$ est l'abaissement de température provoqué par l'addition de 1 gramme de la substance à la masse de solvant employée. On peut l'assimiler à K et écrire: $KM=2A\times\frac{T^2}{L}$. Cette formule montre que la valeur K×M est proportionelle à l'abaissement moléculaire de la tension de vapeur A. Or, A n'est voisin de 0,01 qu'à la condition qu'il réponde à des tensions voisines de 760 mm. d'après Raoult, (loc. citat. p. 46) qui insiste, en écrivant p. 56:

" $M\times\frac{dT}{P}$ dépend essentiellement de la pression atmosphérique, c'est-à-dire de la pression sous laquelle l'ébullition se produit."

Donc le remplacement de A par 0,01, est doublement approximatif, puisque la valeur 0,01 n'est pas rigoureuse et n'est, en outre valable qu'aux environs de la pression atmosphérique.

En résumé, les lois de la cryoscopie et de la tonométrie ne sont pas des lois limites comparables à celles de Mariotte et de Gay-Lussac mais des résultats limités par des conditions expérimentales assez étroites. De sorte que la thermodynamique h'a que des rapports éloignés avec ces phénomènes.

ETAT DES CORPS DISSOUS

Les lois de Raoult expriment, d'après leur auteur, qu'il existe un rapport entre le nombre *n* des particules dissoutes, et le nombre N des particules du solvant. Par exemple, la plupart des corps dissous dans la benzine au taux de 1 molécule dans 100 molécules de solvant, donnent pour abaissement cryoscopique moléculaire 49,[illegible] voisin du nombre $52 = K \times M$, calculé d'après la formule:

$$K.M = 0{,}02 \frac{T^2}{L}$$

Au contraire, le phénol et les acides organiques donnent un nombre deux fois plus petit comme le montre le tableau suivant:

1 molécule phénol dans 100 molécules benzine donne KM = 26

1 molécule monochloracétique dans 100 molécules benzine donne KM = 25,4

1 molécule acide propionoque dans 100 molécules benzine donne KM = 26

1 molécule acide phénylacétique dans 100 molécules benzine donne KM = 24

Raoult, Van't Hoff et tous les autres auteurs, concluent que en solution benzinique, les corps précédents sont bimoléculaires, c'est-à-dire que leur particule dissoute (*dissolécule*), est formée par la juxtaposition de deux molécules simples. C'est là une conclusion nécessaire, si l'on admet que le rapport des particules dissoutes aux particules dissolvantes $\frac{n}{N}$ reste constant.

Les données cryoscopiques et tonométriques conduisant à la nécessité d'admettre que certaines particules dissoutes sont constituées par des molécules condensées, on peut se demander qui la valeur de KM calculée d'après la formule $KM=0{,}02\ \frac{T^2}{L}$ oblige à supposer que la particule dissoute normalement est à l'état moléculaire. Il est facile de prouver le mal fondé de cette hypothèse.

Considérons l'acide acétique. D'après Cahours, la densité moléculaire de vapeur de ce corps se rapproche de la valeur $M^2=(C^2H^4O^2)^2$ à mesure que la température s'abaisse: et elle s'en éloigne à mesure que l'on chauffe ou que l'on détend la vapeur. Donc, à température notablement inférieure à 120°, vers 18°, par exemple, la densité de ce corps correspondra à la formule condensée. La particule liquide, obtenue par compression de la vapeur, sera elle-même bimoléculaire, au moins. On retrouve ainsi la forme que Ramsay et Shields avaient fixée à $(C^2H^4O^2)^2=120$.

Puisque le rapport $\frac{n}{N}$ reste constant pour tout corps cryoscopé dans l'acide acétique, comme N correspond à 2 molécules, il faut que *n* corresponde aussi à 2 M, c'est-à-dire que chaque particule dissoute soit elle-même une particule double. Voici une singulière vérification de cette conclusion.

Si l'action dissolvante de l'acide acétique oblige les corps dissous dans son sein à prendre l'état bimoléculaire, elle agira de la même façon sur les gaz. Par conséquent le poids d'acide chlorhydrique sec, dissous dans 100 molécules d'acide acétique, qui correspondra à la valeur normale 39 de K.M sera, non pas $H\,Cl=36{,}5$, mais $H^2Cl^2=71$. L'expérience sanctione cette prévision. Donc:

Les corps dissous dans l'acide acétique y prennent normalement la forme bimoléculaire.

Sous cette condition seulement, la formule $K.M=0{,}02\ \frac{T^2}{L}$ permet de calculer le poids moléculaire M du corps dissous; mais le poids de la particule dissoute M′ s'obtiendra en remplaçant M par $\frac{M'}{2}$ dans la formule précédente et répondra au coefficient $K'=\frac{K}{2}$.

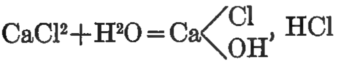
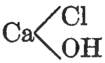
Tout porte à généraliser cette conclusion. En effet, d'après Raoult, l'eau dissoute dans l'acide acétique donne un abaissement normal, c'est-à-dire que son poids moléculaire 18 répond à la valeur 39 normale de K.M calculée pour l'acide acétique. Donc l'eau, comme les corps organiques, comme les chlorures métalliques anhydres, est bimoléculaire en solution acétique.

L'inverse semble absolument logique, non seulement par raison de réversibilité, mais pour ce motif qu'en dissolvant l'acide acétique liquide dans l'eau en excès, il n'y a pas d'effet thermique sensible. La cohésion seule de l'acide acétique liquide $(C^2H^4O^2)^2$ parait donc être modifiée par ce solvant; car s'il y avait dédoublement moléculaire, suivi d'une expansion des molécules simples $C^2H^4O^2$ dans le liquide, ce double effet nécessiterait une double absorption de chaleur.

Alors l'acide acétique dissous dans l'eau, donnant comme le sucre la valeur normale $K.M=19$ propre à ce solvant, les dissolécules de ces deux corps y sont bimoléculaires. Au contraire, celles du gaz chlorhydrique donnant la valeur 38 correspond à une dissolécule HCl monomoléculaire, et non plus à $\frac{1}{2}$ HCl.

Dans cet ordre d'idées l'eau est un solvant comme un autre, et les remarquables expériences de M. Harry Jones, de Baltimore, trouvent une nouvelle explication. Par exemple, si l'abaissement moléculaire du point de congélation de $CaCl^2$ est 4 fois plus grand que celui qui résulte de la formule de Van't Hoff, c'est que:

1o. $CaCl^2$, comme NaCl, comme HCl, est monomoléculaire en solution, c'est-à-dire qu'il correspond normalement au produit $KM=38$;

2o. Au contact de l'eau, le chlorure s'hydrolyse manifestement car $CaCl^2$ ne peut plus s'extraire de la solution. Admettons que  $CaCl^2+H^2O=Ca\left\langle\begin{matrix}Cl\\OH\end{matrix}\right., HCl$ les deux molécules  $Ca\left\langle\begin{matrix}Cl\\OH\end{matrix}\right.$ et HCl agissant comme 2 HCl sur le point de congélation, produiront un abaissement 4 fois plus grand que celui des corps organiques auxquels s'applique la formule de Van't Hoff.

CHAPITRE II

LES FORMULES RATIONNELLES

J'ai dit ailleurs et ici pourquoi ces formules de Van't Hoff sont plutôt des formules approximatives que des formules rationnelles, c'est-à-dire rattachées indubitablement aux deux principes fondamentaux de la thermodynamique.

Il n'en est pas de même de la loi de l'action de masse, qui est considérée aujourd'hui comme intangible. Pourtant la formule qui résume cette loi n'est pas à l'abri de la critique.

Depuis Guldberg et Waage, elle a pour forme:

$$\frac{\mathrm{p^m p'^{m'}_{\cdots}}}{\mathrm{q^n q'^{n'}_{\cdot\cdot}}} = \text{Constante}$$

en appelant: $p\ p'$ .... $q\ q'\ q''$ ....les pressions partielles des corps $\chi\ \chi', \chi'',$ .....$\gamma, \gamma', y'',$.....qui sont en équilibre sous la condition: $m\chi + m'\chi' + m''\chi'' = n\gamma + n'\gamma' + \ldots\ldots$

M. Le Chatelier, analysant les résultats énoncés par Van't Hoff concernant la loi de l'action de masse et celle du déplacement de l'équilibre, est arrivé aux mêmes conclusions que le savant hollandais "par des considérations purement expérimentales," dit-il dans son Mémoire sur les *Equil. Chimiques.* (*Annales des Mines*, 1888 p. 109, 219 et 225.)

On sait que c'est sur l'artifice des parois semiperméables, découvertes par Traube et utilisées par Pfeffer, que Van't Hoff a basé sa démonstration rationnelle.

Appliqué à l'équilibre suivant:

$$4HCl + O^2 = 2H^2O + 2Cl^2,$$

le raisonnement de Van't Hoff est irréprochable dans les limites de température où les vapeurs H^2O et HCl existent sans décomposition; Il ne l'est plus pour les phénomènes de dissociation.

Précisément, c'est " en généralisant les conséquences déduites d'expériences de dissociation trop peu nombreuses" faites par Deville, Isambert et M. Lemoine, que M. Le Chatelier cite la formule générale:

$$\frac{\mathrm{p^m\ p'^{m'}}}{\mathrm{q^n\ q'^{n'}}} = \mathit{Constante}$$

qu'il applique aussitôt à la dissociation du gaz carbonique:

$$2CO + O^2 = 2CO^2$$

et à celle du bromhydrate d'amylène (loc. cit. p. 109, 110), quoique, encore une fois, ni l'expérience ni la théorie n'autorisent cette généralisation.

Montrous d'abord expérimentalement que la formule précédente ne s'applique pas à la décomposition du bromhydrate d'amylène à température constante.

En prolongeant l'action de la température pour obtenir les densités du corps à l'état dissocié, M. Lemoine a observé pour l'équilibre:

$$\begin{array}{c} \underline{C^5H^{11}B_2 = C^5H^{10} \times HB_2} \\ q \qquad\qquad p \quad\; p' \end{array}$$

les fractions de décomposition suivantes:	à 175,°	à 185°,	à 200°,
sous la pression atmosphérique H	0,05	0,28	0.50,
sous la pression réduite a 1/10H	0,28	0,54	0,69

Si l'on calcule $\frac{pp'}{q}$, ici $\frac{p^2}{q}$ = *Constante* =, on trouve que *pour la fraction 0,05 la constante est proportionnelle à 6,57; et pour la fraction 0,28. la constante proportionnelle à 27,2.*

Donc, à 175,° ces deux valeurs de la constante sont très différentes. A 185,° elles sont proportionnelles à 27 et à 158, c. a. d. fort éloignées.

De même, dans la série des essais à 185°:

pour la fraction 0,50, la valeur de la constante est	1250,
pour la fraction 0,69, elle devient	384.[1]

Ces différences inadmissibles entre des nombres qui devraient être égaux, résultent de ce que la démonstration de Van't Hoff ne s'applique pas aux phénomènes de dissociation,

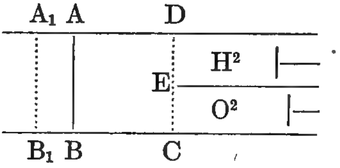
Je vais le prouver.

Dans la décomposition du gaz chlorhydrique par l'oxygéne, la théorie est admissible parce que les vapeurs H^2O et HCl ne sont pas décomposées à la température de l'équilibre. Mais supposons de l'eau dissociée dans le réservoir ABCD = V sous la pression totale P à T°. Appelons q,p et p' les pressions partielles de la vapeur, de l'hydrogéne et de l'oxygéne dans le mélange. Les pointillés CE et DE figurant des parois semiperméables: la première à l'hydrogéne, la seconde à l'oxygéne.

---

[1] Lemoine Compt Rend 20 avril 1891.— Reprenant ces expériences dans la vapeur d'al aniline c.a.d. à 182°, j'ai verifié qu'il fallait 2 heures environ pour obtenir l'équilibre de dissociation et constaté qui à cette température sous la pression 750 mm. la fraction djoulé était 26,5%. C'est une bonne verification des idées et des expériences de M. Lemoine.

Je comprime des gaz séparément dans les cylindres H^2 et O^2



sous une pression très peu supérieure à p et à p' en même temps que je retire H^2O sous la pression q par le fond AB perméable à la vapeur. Je ne change rien, à aucun moment, dans le réservoir ABCD. Si la vapeur H^2O passée dans l'espace ABA_1B_1 conservait sa pression partielle q, l'opération inverse de ferait d'une façon réversible et le raisonnement de Van't Hoff continuerait à s'appliquer; mais l'espace ABA_1B_1 étant lui aussi à la température T°, la vapeur d'eau qui pénètre dans cet espace, sous la pression q se dissocie et ne conserve pas cette pression. La réversibilité du cycle isotherme de Van't Hoff est par conséquent détruite dès cet instant.

Pour parer à cette faute que j'ai souvent signalée, et en particulier dans ma "*Contribution a l'histoire de la Chimie,*"[1] on peut supposer que AB est un piston plein et non plus une paroi semiperméable. En déplaçant ce piston sous la pression totale P, on reconstitue et l'on défait à volonté la molécule d'eau dissociée par une suite d'opérations qui sont toutes réversibles.

Toutefois quand on passe d'un état [P, V, T] figuré par ABCD = V, à l'état $[P_1, V_1, T]$ figuré par A_1B_1 $CD = V_1$, par exemple, le travail nécessaire pour revenir de A_1 B_1 à AB a encore pour expression

$$\int VdP$$

Seulement, comme on ignore ici la relation qui unit P à V, ce travail ne peut s'exprimer en fonction de P, V, P_1 et V_2. Il dépend des conditions de l'expérience. Pour toutes les phases du cycle ci-dessus proposé, il a pour valeur:

$$P_1V_1 - P.V + \int V.dP - \lg \frac{p_1{}^{m}}{p^{m}} - \lg \frac{p'_1{}^{m'}}{p_1{}^{m'}}$$

[1] Hermann Edit. 1910.

Puisque la valeur de $\int$ ne peut s'exprimer en fonction de P, V ou V_1 et P_1 il ne parait pas que $P_1 V_1 - PV + \int VdP$ soit égal à $\lg \frac{q_1 n}{qn}$ avec $q = P - p_1 - p$

Si l'on objectait que la démonstration de Van't Hoff n'est pas la seule, et que l'on peut arriver à la formule de Guldberg et Waage par l'hypothèse que l'entropie d'un système égale la somme des entropies de ses parties, il resterait deux points à élucider:

1o. Dire pourquoi les cycles fondés sur les parois semi-perméables conduisent à la loi des masses dans certains cas et non pas dans d'autres,

2o. Prouver que l'hypothèse basée sur l'entropie est un axiome irréfutable; ce que beaucoup de mathématiciens mettent en doute, et ce qui n'est peut être pas conforme à l'expérience, car voici des faits:

Cahours en traitant les éthers salicyliques par la chaux vers 250°, a obtenu des oxydes mixtes

I $CaO + C^6H^5O.CO^2C^2H^5 = CaCO^3 + C^6H^5 - O - C^2H^5$

Au point de vue mécanique et chimique, cette réaction semble déterminée par l'affinité de la chaux pour le gaz carbonique. Cette affinité répond à un dégagement de chaleur de 44000 calories

II $CaO + CO^2 = CaCO^3 + 44.000$ *cal.*

Cependant, bien que la chaux se combine à CO^2 dans ces conditions, j'ai constaté qu'avec de la chaux en grains, cette base n'intervient pas. On obtient à 225°.

III $C^6H^5O.CO^2.C^2H^5 = C^6H^5 - O - C^2H^5 + CO^2$

J'ai pu recuiellir, en opérant avant le refroidissement complet des tubes, des proportions de gaz CO^2 libre qui, par rapport au gaz combiné, dépasse parfois le rapport: $\frac{95}{5}$ c. a. d. CO^2 *libre* 95%; CO^2 *combiné* 5% (dosage)

Donc l'énergie totale dépensée dans la réaction I qu'on la considere sous forme de chaleur totale de combinaison (Berthelot), ou de chaleur non compensée (Helmoltz—Clausius,) ou d'entropie (Gibbs), n'est pas la cause de la réaction I.

En d'autres termes, cette énergie totale n'est pas la résultante de la somme des énergies correspondantes aux réactions II et III et quoique la chaux se combine à CO^2 dans les circonstances de la réaction, cette énergie additionnelle n'est ni prépondérante ni déterminante.

CONCLUSION

Les théories basées sur l'assimilation de la molécule gazeuse & de la particule dissoute, & celles qui reposent sur la loi de l'action de masse, ne doivent pas être acceptées sans réserve.

A NEW METHOD OF MEASURING THE PRESSURE OF CORROSIVE GASES AT CONSTANT VOLUME

By George Shannon Forbes and Leslie Briggs Coombs
Harvard College, Cambridge, Mass.

Serious experimental difficulties are encountered in measuring the pressure of corrosive gases at constant volume and at high temperatures. The manometer devised for this purpose by Ladenburg and Lehmann[1] was a flattened quartz tube bent in the form of a Bourdon pressure gauge and provided with a pointer moving over a scale. This was used by Bodenstein and Katayama[2] in measuring the dissociation pressures of sulphuric acid and of nitric oxide. The behavior of this device is most exasperating, as one of the authors of this paper can testify from personal experience; it requires careful calibration; lastly, it is expensive and withal extremely fragile. Johnson's modification[3] of this manometer was a flattened glass tube coiled in a spiral, and terminated by a mirror. This spiral was enclosed in a mantle within which the pressure could be varied at pleasure. The mirror remained stationary so long as the external pressure on the spiral equalled the internal pressure. If a manometer is to contain a liquid, that liquid must have no appreciable vapor pressure of its own at the temperatures employed, and must not dissolve or react with the gases with which it is in contact. Neither mercury, sulphuric acid, glycerine, nor any other liquids hitherto employed can meet these requirements in dealing with vaporized acids, halogens and similar substances at high temperatures.

The present apparatus is easily constructed from materials available in every laboratory. The pressure gauge is outside the oven, and its manipulation is easily mastered. No calibration is required. It is adapted for demonstration or research on pressures of gases and vapors, as well as vapor pressures of liquids and solids, which otherwise could be studied only by quartz or glass manometers or by methods similar to those of Dumas or Victor Meyer.

---

[1] Ber. d. deutsch. physik. Ges., *4*, 20 (1906).
[2] Z. Elektrochem., *15*, 244 (1909).
[3] Z. physik. Chem., *61*, 457 (1908).

The construction of the apparatus is evident from the diagram. The gas or vapor is contained in a bulb *A*, of any desired shape, and about 250 cc. in capacity. The bulb may be made of hard glass if necessary. Its stem *B* is sidenecked by a tube *C*, three millimeters in internal diameter and bent horizontally just above the point where it emerges from the electric oven *E*. This tube is wound rather closely with fine nichrome ribbon from *D* up to and beyond *G*. The small bulb *F* is filled before the determination with a finely powdered mixture of an equimolecular mixture of fused lead and silver chlorides. Various other pure or mixed salts could of course be used instead. This mixture was found to melt at about 350 degrees, that is, 140 degrees below the melting point of either of the pure chlorides. The tube is constricted at *H*, and the volume of this part of the system is further diminished by a section of glass rod *I*. An additional section may be introduced between *H* and *G*. The small connection *J* of vacuum tubing contains a smooth glass pearl which acts as a gas-tight seal unless the tubing is pinched at that point. A section of thermometer tubing *K* prevents any rapid flow of air in either direction. A fine capillary *L* which can easily be broken and sealed up again makes it possible to admit air or expel it from this part of the apparatus. Adjoining is a manometer provided with a flexible tube *N*; by raising or lowering the open tube *P* any pressure may be produced at *O*. This pressure is found by combining the barometric pressure with the difference in level between the mercury surfaces *O* and *Q*, which is read from the millimeter scale *S*. The readings of both barometer and manometer can be reduced to zero Centigrade by reference to tables.

If the pressure of the vapor of a liquid, as phosphoryl chloride, or of a solid, as iodine, is to be measured, a weighed amount is sealed up in a weighed capsule of glass tubing provided at one end with an exceedingly fine closed capillary. The stem *B* is held horizontally and the capsule allowed to slide in until the capillary is inserted in the small tube *T* fused into the bottom of the bulb. The bulb is evacuated to a few millimeters through the stem which is then fused off at some intermediate point. The chlorides in *F*, about one gram in weight, are carefully fused with a small flame, and the horizontal tube *FG* inclined by raising the bulb. The liquid runs toward *G* and easily forms a " drop " about one centimeter in length. Its small size and high temperature will preclude the solution of an appreciable amount of the gases in contact with it, judging by analogy from many researches carried out in the Harvard laboratory. A current barely sufficient to keep it in fusion is passed through the nichrome ribbon. The pressure of the residual air in *A* is now determined if necessary. The level in tube *P* is adjusted until on pinching the rubber tube *J* over the pearl, no movement of the drop is observed. Violent movements of the drop are rendered impossible by the great friction of the air in the thermometer tubing K. The drop easily responds to pressure changes of one or two-tenths of a millimeter in the manometer. Therefore the pressure in *A* can be equated exactly to the pressure at *O* unless the surface tension on opposite sides of the drop differs by reason of inequalities in temperature or the dissolving of gases. The first possibility is obviated by uniformity in the winding; the second seems unlikely in view of the small tendency of fused salts to dissolve gases, as already pointed out. Any other pressure in *A* can be determined in the same manner. The capsule containing the liquid is next broken by gentle shaking at a temperature where its vapor pressure does not exceed the pressure of the residual air (or nitrogen) in *A*. If a gas is to be investigated, it is admitted slowly into the evacuated bulb through a well-ground stopcock, and the drop is kept stationary by forcing in through *J* the proper amount of air. The same manipulation is carried out when the pressure of a gas or vapor is increased by raising the temperature of the oven. As the volume between the drop and the glass pearl is very small, the drop will not fall into *G* even if the valve in *J* is very carelessly manipulated while the pressure in *A* is increasing.

The pressure of the substance introduced is equal to the compensating pressure at *O* with two corrections. First, the pressure of the residual air or nitrogen at t^1, multiplied by the ratio $\frac{T^2}{T^1}$ must be subtracted. The second correction is necessitated by the fact that all the gas is not at the same temperature. Let V equal the total volume of the system and v the volume of the section *DR* of the tube *C*, in which the temperature is kept constant at t^1 by the nichrome wire. Imagine now the volume v reduced at the observed pressure p from t^1 to t, the temperature of the bulb. The gas will now occupy the volume $V - v \frac{t^1 - t^{11}}{t + 273}$. Now change the volume of the gas, at constant and uniform temperature t, back to V again when it will attain the pressure P.

$$P = p \frac{V - v \frac{t^1 - t}{t + 273}}{V} = p - \left[p \cdot \frac{v}{V} \cdot \frac{t^1 - t}{t^1 + 273} \right]$$

The term in the bracket is the correction which must be subtracted from the observed pressure p to obtain P, the pressure which would be exerted by the same body of gas in the same volume in case the temperature of the bulb prevailed also in the tube wound with nichrome. For the values of V, v and t^1 in the apparatus described below, the correction never exceeded one millimeter.

The practicability of this method was established by determinations of the pressure of air and of chlorine, heated at constant volume to various temperatures. The oven used was cylindrical and was wound uniformly with several layers of nichrome ribbon insulated by asbestos. The temperature was controlled by a variable external resistance, and ample time was allowed to get a real equilibrium of temperature. Circular disks of asbestos accurately fitting the walls of the oven were fastened to the top and bottom of the bulb to keep that part of the oven uniform in temperature. The top and bottom of the oven also were protected by several thicknesses of asbestos. The temperature was measured by a suitably annealed thermo-couple of iron and constantan insulated from each other up to the junction by a glass tube. The terminals were plunged into tubes of mercury supported in a beaker of water whose temperature was read to tenths of degrees. The electromotive force was measured by the compensation method on a potentiometer so adjusted that when the terminals were at 25°, and the junction protected by a glass jacket was kept at

445° by sulphur vapor boiling under 760 mm., exactly 420 ohms on the potentiometer had to be included between the terminals to bring the d'Arsonval galvanometer to rest. An effort was always made, while measuring pressures, to halt the temperature of the oven at points where interpolation was unnecessary. Thus degrees were read directly from the apparatus and added to the temperature of the terminals. The readings were independent of the depth of immersion of the couple. The range between 25° and 445° was explored by readings in steam (100°), aniline (184°), nitrobenzene (209°), and diphenylamine (302°). The calibration of each of the two couples used was checked at frequent intervals. A curve was constructed showing the corrections necessary in order to reduce potentiometer readings to true temperature differences. The temperature at different points on the surface of the bulb was investigated and appeared to be constant within a degree. Still it was felt that the corrected temperatures might differ from the average temperature of the bulb by two or three degrees, and this difficulty, rather than errors in measuring pressures, is believed to be responsible for such irregularities as exist in the results given below.

Three independent experiments were carried out with air and three with chlorine. The results, exhibited in the table, show the practicability of the method.

V, the volume of the bulb and side tube back to the drop, was 260 cc., the stem *B* being sealed off each time at the same distance from the bulb.

v, the volume of the gas in the section *DR* (15 cm. long), as determined by weighing mercury in a measured section of the tube, was 1.3 cc.

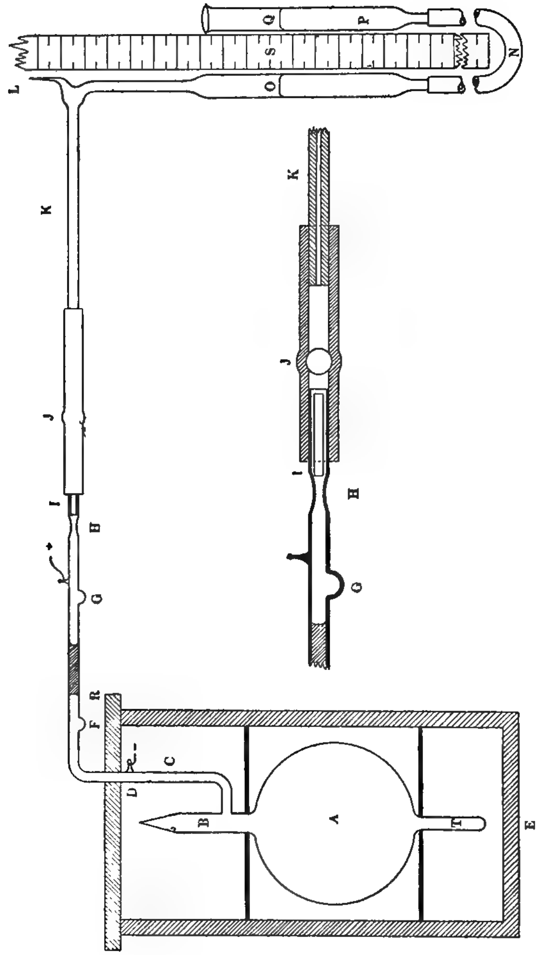
t^1, the average temperature of v, as determined by a thermo-couple inserted in the tube in a special experiment, was 330 degrees.

T is the absolute temperature of the bulb found by adding 273 to the corrected readings of the thermo-couples..

p represents the pressure indicated by the manometer.

P is the same corrected for lack of uniformity in temperature as previously described.

The pressure P_x is calculated from P_n the pressure at t_n by the formula $P_x = P_n \cdot \frac{T_x}{T_n} \cdot (1+0.000028\,[t_n - t_x])$ where 0.000028 is the


L
K
J
I
H
G
+
R
F
C
D
B
A
T
E
O
S
Q
P
N
K
J
I
H
G

value assumed for the mean coefficient of cubical expansion of soda lime glass at the temperatures noted.

All the measurements made are included in the table, except one, where time was lacking to reach a constant temperature, and one rejected for unknown but obviously gross error. It is interesting to note that the figures show the abnormally large increase in the temperature coefficient of chlorine at temperatures below 100°.

EXPERIMENT 1. (AIR)

tobs.	T corr.	pobs.	P corr.	P calc.
18	291	213.2	212.6	213.7
183	454	329.5	329.1	331.8
223.5	491.5	361.5	361.2	358.9
254	522.5	381.5	381.2	.....

EXPERIMENT 2. (AIR)

tobs.	T corr.	pobs.	P corr.	P calc.
21	294	207.5	207.0	206.2
265	532	370.4	370.2	370.7
287	554	385.0	384.8	385.4
308	575	399.5	399.4	399.6
328	595	413.5	413.5	413.4
348	616	427.5	427.5	427.9
362.5	631	438.0	438.1	.....

EXPERIMENT 3. (AIR)

tobs.	T corr.	pobs.	P corr.	P calc.
20	293	247.5	246.9	247.9
141.5	414.5	349.0	348.4	349.5
182	453	382.5	382.0	381.6
223	491	415.5	415.2	413.3
263.5	530.5	446.3	446.0	.....

EXPERIMENT 4. (CHLORINE)

tobs.	T corr.	pobs.	P corr.	P calc.
26.5	299.5	384.0	383.0	388.3
117.5	390	503.0	502.4	504.4
148	419.5	542.0	541.2	542.5
178.5	449	580.0	579.3	579.8
209	479	615.5	614.9	613.9
239	506	653.1	652.6	.....

EXPERIMENT 5. (CHLORINE)

tobs.	T corr.	pobs.	P corr.	P calc.
123	395.5	518.0	517.1	515.5
173.5	444	580.6	579.8	578.1
224.5	491.5	643.0	642.8	638.6
254.5	521.5	680.7	680.2	677.3
285	552	718.7	718.4	716.6
315.5	583	756.5	756.4	.....

EXPERIMENT 6. (CHLORINE)

tobs.	T corr.	pobs.	P corr.	P calc.
23	296	387.1	386.1	388.5
82	355	464.6	463.7	463.9
103	375	489.8	488.9	490.2
133.5	404	528.7	527.9	527.8
164.5	434	565.5	564.7	566.0
205	471.5	615.1	614.5	.....

In closing, it is a pleasant duty to acknowledge the courtesy of Simmons College, in whose laboratory a part of the work was carried out.

EQUILIBRIA IN SYSTEMS CONTAINING ALCOHOLS, SALTS AND WATER, INCLUDING A NEW METHOD OF ALCOHOL ANALYSIS

By Geo. B. Frankforter and Francis C. Frary
University of Minnesota, Minneapolis, Minn.

The work of which this is abridged report,[1] was conducted with the primary purpose of studying the salting out of alcohol by potassium fluoride, and using the results as the basis of a method for the determination of alcohol. Aside from the work thus indicated, several other systems involving alcohols, salts and water were studied for comparison.

As one of the important phases of the problem there arose the question of the dehydration of the alcohol by potassium fluoride, as a matter of industrial importance.

The alcohols differ among themselves in their behavior toward salting-out reagents. It appears in general that the higher the molecular weight of the alcohol, the easier it is to salt it out. Potassium carbonate is the only salt known which has the power of salting-out methyl alcohol (Linebarger, Am. Chem. J., 1892, *14*, 381), while the carbonates, phosphates and hydroxides of sodium and potassium, the sulphates of sodium, ammonium cadmium, manganese, iron (ferrous), cobalt, nickel, magnesium and zinc, the nitrates and citrates of ammonium and potassium, sodium thiosulphate and silicate are all capable of producing two layers in ethyl alcohol under certain conditions. A very much larger number of salts precipitate propyl alcohol, and the higher

[1] For complete report see Research Bull. 1 of the University of Minnesota, which will be issued and may be obtained by applying to the President of the University.

(Firnhaber, Archiv des Apothekervereins Norddeutschland, 1824, *7*, 151; Linebarger, loc. cit., Brandes, Pogg. Ann., *20*, 586; Schiff, Lieb. Ann., *118*, 362; Procter, Chem. News, 1864, *9*, 25; Parmentier, Compt. rend., *104*, 686; Traube und Neuberg, Z. physik. Chem., 1887, *1*, 509; Bodländer, Z. physik. Chem., *7*, 308; Dodge and Gratton, J. Physik. Chem., 1898, *2*, 498; de Bruyn, Z. physik. Chem., 1900, *32*, 64; Ketner, Z. physik. Chem., 1902, *39*, 641; Fleckenstein, Physikal. Zeit., 1905, *6*, 419.)

alcohols are not miscible with water and hence are still more readily and completely salted out. The salting-out of ammonia by potassium carbonate or silicate (Procter, Chem. News, 1864, *9*, 25; Newth, J. Chem. Soc., 1900, *77*, 775) is the only example of the same phenomenon that I have found in the case of inorganic liquids, but among other organic liquids it is common.

The dehydration of alcohol by different salts has been studied by many chemists.

Of the various substances used, the commonest is lime, which gives a very strong alcohol, but causes quite a loss and is inconvenient on account of the large quantities of lime used.

The general theory of the drying action of a salt on a liquid, and the importance of choosing a salt which takes up a large proportion of its weight in water, has been discussed by Foote and Sholes (loc. cit.). Of the salts which can give a product containing over 97% alcohol, lime takes up over 32% of its weight of water, anhydrous copper sulphate 11%, anhydrous zinc sulphate 11%, magnesium sulphate 15%, barium chloride 7.7%, and potassium carbonate 13%. According to the results of Foote and Sholes, the lowest hydrates of these substances are in equilibrium with 99.5, 99.5, 99.4, 98.4, 99.3% alcohol respectively, at 25°. Potassium fluoride, absorbing 62% of its weight of water to form the lowest hydrate, and being in equilibrium at this point with 97.5% alcohol, certainly deserves to rank well among drying agents for liquids miscible with water. On account of its greater solubility, apparently, it absorbs the water and comes into equlibrium with the solution much more rapidly than most of the other drying agents.

For drying organic liquids, it is often convenient to use a sat

(Soubeiran, Ann. 1839, *30*, 356; Mendeleef, Z. f. Chem., 1865, 260; Erlenmeyer, Ann., *160*, 249; Smith, Chem. News, *30*, 235; Lescoeur, Bull. soc. chim., 1897, (3), *17*, 18; Yvon, Compt. rend., 1897, *125*, 1181; Ostermeyer, Pharm. Zeit., *43*, 99; Z. anal. Chem., 1900, *39*, 654; Vitali, Boll. chim. farm., *37*, 257; Z. anal. Chem., 1900, *39*, 46; Bull. Chem. Zeit., 1900, *24*, 814, 845; Young, J. Chem. Soc., 1902, *81*, 707; Evans and Fetsch, J. Am. Chem. Soc., 1904, *26*, 1158; Winkler, Ber., 1905, *38*, 3612; Elektrochem. Werke Bitterfeld, Brit. Pat. 31, 567, Sept., 1906, and Ger. Pat. 175, 780, Sept. 1905; Klason and Norlin, Arkiv. Kem. Min. Geol., 1906, *2*, 1, J. Chem. Soc., 1906, *90*, i, 921; Kailan, Monatsh., 1907, *28*, 927; Plücker, Z. Nahr. Genussm., *17*, 454; Pozzi-Escot, Bull. assoc. chim. sucr. dist., *26*, 580; Hess. U. S. Pat. 996, 763; Chem. Fabr. Griesheim Elektron, Ger. Pat. 236, 591; Foote and Sholes, J. Am. Chem. Soc., 1911, *33*, 1309.)

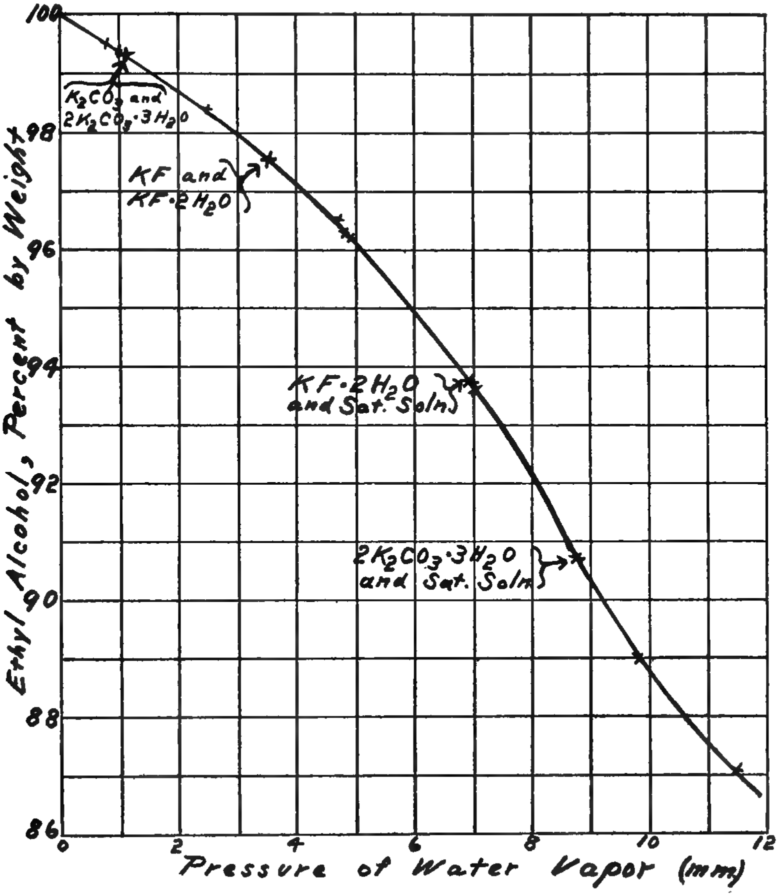


Figure 1
EQUILIBRIA BETWEEN ALCOHOL, WATER VAPOR, AND SALTS

urated solution of potassium carbonate. It gives less opportunity for loss of the liquid, mechanically, and the equilibrium is quickly reached. Any salt which is to be suitable for this purpose must have a good salting-out power, so that little of the liquid shall dissolve in it, and its saturated solution must have a low vapor tension. With the exception of the hydroxides of sodium and potassium, and potassium carbonate, the salts above mentioned

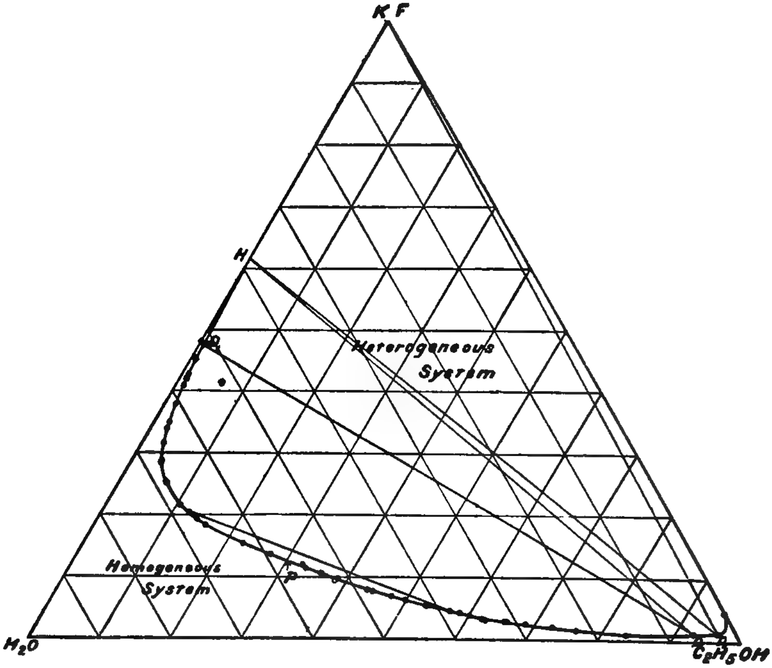


Figure 2
EQUILIBRIUM IN THE SYSTEM: POTASSIUM FLUORIDE, ETHYL ALCOHOL AND WATER

as having sufficient salting-out power to affect a solution of ethyl alcohol are not deliquescent, in their hydrated form, so the vapor pressure of the crystalline hydrate must be relatively high, and that of the saturated solution would be higher. By plotting the results of Foote and Sholes, the curve shown in Figure 1 is obtained, showing the vapor tension of the water in strong alcohol. The solutions of alcohol with which saturated solutions of potassium carbonate and fluoride and the solid hydrates are in equilibrium, when plotted on this curve give the approximate value of their vapor tension. It will be seen that while the vapor tension of the hydrate of potassium carbonate is lower than that of the hydrate of the fluoride, the saturated solution of the latter has a lower vapor tension than that of the former, and hence is a better

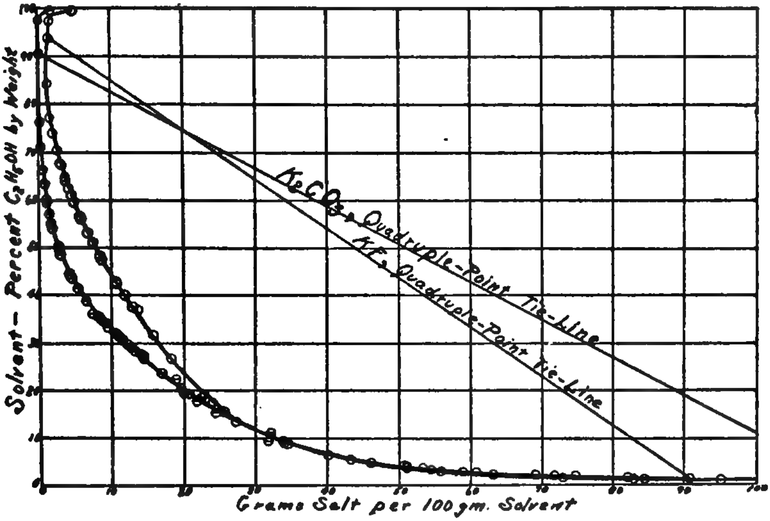


Figure 3

EQUILIBRIA IN SYSTEMS: POTASSIUM FLUORIDE, ETHYL ALCOHOL, WATER, AND POTASSIUM CARBONATE, ETHYL ALCOHOL, WATER, PLOTTED IN RECTANGULAR CO-ORDINATES

drying agent. From this curve it appears that, neglecting the effect of the small amount of dissolved potassium fluoride on the vapor tension of the alcohol, the vapor tension of the saturated aqueous solution of the fluoride is 6.9 mm. and that of the solid hydrate, 3.5 mm.

The salting-out properties of potassium fluoride seem never to have been mentioned in the literature, although they must have been noticed by Berzelius (Pogg. Ann., *1*, 11) who first described it, and by Rose (Pogg. Ann., 1842, *55*, 538) who precipitated some of the salt from solution as the hydrate by addition of alcohol.

The hydrate which this salt forms was first identified by Rose (loc. cit.) as $KF.2\,H_2O$; and Guntz (Ann. chim. phys., (6), *3*, 17) Fremy, (Ann. chim. phys., (3) *47*, 27) Mylius and Funk (Ber. 1897, *30*, 1716) and de Forcrand (Compt. rend. *152*, 1073) have verified the formula. The latter author has shown the existence of a hydrate $KF.4H_2O$ formed below 20°, and melting at 19.3°, while the other hydrate melts at 41°.

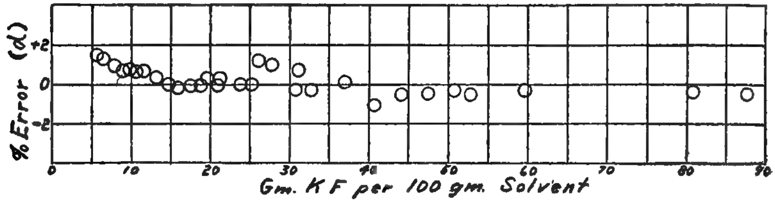


Figure 4
ERROR IN THE DETERMINATION OF ETHYL ALCOHOL IN THE PRESENCE OF METHYL ALCOHOL

Aside from the work above-mentioned, there is very little literature on neutral potassium fluoride.

The precipitation of a liquid from water by the addition of a salt comes under the general class of equilibria in ternary mixtures where the existence of two liquid phases is possible. The general theory of such systems, and the form of the isotherms obtained, have been discussed by Schreinemakers. (Z. Phys. Chem., 1897, *22*, 93, 515; *23*, 649.) There are four classes into which such equilibria are divided: (1) each of the three components forms a binary system having two liquid phases when mixed with either of the other components, (2) two liquid phases are found in two of the possible binary systems above-mentioned, but not in the third, (3) in only one of the binary systems can two liquid layers appear, (4) each component, mixed with either of the others, gives a system with only one liquid phase, *i. e.*, a solution of one in the other, and only when all three are present can two liquid phases exist. All the above classes refer of course to stable systems, and examples of each class have been studied. The salting-out of the alcohols here treated comes under the fourth class, since neither in the system alcohol-water, alcohol-salt (free from water) nor water-salt can two liquid layers be formed, but when all three are present in certain proportions, such layers are formed within certain limits of temperature. It is customary to represent the

(F. W. Clarke, Am. J. Sci., (3), *13*, 291; Kohlrausch, Wied. Ann., 1879, 1; Guntz, Compt. rend., *97*, 256; Tamman, Wied. Ann., *24*, 530; Petersen, Z. phys. Chem., *4*, 384; Ditte, Compt. rend., 1896, *123*, 1281; 1897, *124*, 29; Pauli, Z. Elektrochem. 1897, *3*, 474; Tanatar, Z. anorg. Chem., 1901, *28*, 255; Fox and Herz, Z. anorg. Chem., 1903, *35*, 129; Karadeef, Centr. Min., 1909, 728; C. A., 1911, *4*, 433.)

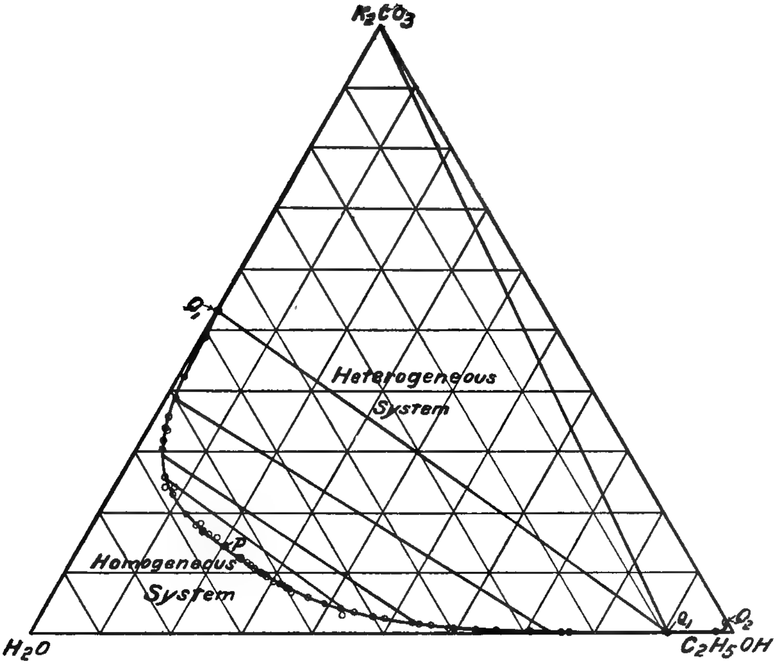


Figure 5
Equilibrium in the System: Potassium Carbonate, Ethyl Alcohol, and Water

equilibrium in such ternary systems in triangular co-ordinates, and the theory of such representation is too well known to require repetition.

EXPERIMENTAL METHODS

The Binodal Curve. The point at which an inhomogeneous solution of the alcohol, salt, and water just become homogeneous, is a point on the binodal curve, and the determination of a number of such points enables one to plot this curve accurately. For the purposes of this investigation a synthetic method of determination was chosen, rather than an analytical one, as it appeared to be more rapid and also much more accurate. To make a series of such determinations, an Erlenmeyer flask fitted with a ground stopper was cleaned, dried, and weighed, and the dried salt weighed into it. In the case of potassium fluoride, the salt has been ignited and weighed in a covered platinum crucible and was simply transferred to the flask, and the crucible rinsed out to get the last traces. This method was adopted to avoid the absorption of water by the salt during the transfer and weighing. It was found that the amount of moisture absorbed while weighing the salt in the covered crucible was only about a tenth of a milligram per minute. After weighing the salt, water was added to dissolve it, the flask again weighed, and enough alcohol added to cause the formation of two layers. A trace of the solid dye used as indicator was now added, and the flask again weighed. Water was now added from a burette, with shaking, until the solution just became homogeneous, the flask weighed again, and the addition of alcohol and water repeated until a series of results was obtained.

All weighings were made on a Sartorius balance of ample capacity easily sensitive to 0.5 mg. with a load of 500 gm. on each pan, but weighings were only made to the nearest milligram. It is not claimed that the accuracy of the titration was generally greater than 0.1 or 0.2 gm., but the weighing was carried to milligrams to minimize cumulative errors in the quantities of alcohol and water present. When the flask had to stand long enough during a series to lose appreciably in weight, corrections were always made for such loss, which generally amounted to less than 30 mg. None of the flasks used showed any signs of etching by the fluoride, and weighing before and after use showed that the loss by such etching, and hence the contamination of the solution, were negligible.

Spirit Blue was used as an indicator, and gave very good results, except with potassium carbonate, which bleached it quickly. Phenol phthalein was later used with this salt, a few minute crystals of the solid being sufficient. The function of the indicator was to color the alcoholic layer, and render it easily visible when only a trace of it was present.

No attempt was made to work in a thermostat, or to control the temperature closer than two or three degrees, for two reasons. In the first place, preliminary experiments with potassium fluoride and ethyl alcohol showed the effect of such changes in temperature to be negligible, and in the second place such control would not be practical in the use of the figures obtained as the basis for an analytical method, and the possibility of obtaining accurate determinations under such conditions could most easily be determined by running a number of series under ordinary laboratory conditions, and comparing the points found. With propyl alcohol, where temperature was found to exercise more influence, more care was taken to control the temperature. The heat of the hands and the heat of dilution of the salts and alcohol tended to keep the temperature a little above that of the laboratory, and when not otherwise stated, the temperature of the solution may be assumed to have been between 23 and 26°C. Care was taken to avoid loss by evaporation or other causes during the course of the determination.

Specific Gravity Determinations. These were all made with 50 cc. pycnometers which had been carefully calibrated by correcting the thermometer against a certified thermometer graduated to 0°.02, and weighing full of water with all the usual precautions. The ground joints connecting the thermometer and capillary to the flask were tight, and by taking care to get the temperature of the room to within a degree of that of the substance to be weighed, it was easy to get very concordant results, duplicates generally agreeing to about 0.00005.

Hehner's table for ethyl alcohol and Dittmar and Fawsett's for methyl alcohol were used. For weak solutions of propyl alcohol the recent table of Doroshevskii and Rozdestvenskii (J. Russ. Phys. Chem. Soc., *41*, 1428; C. A., 1911, *5*, 409; Chem. Zentr., 1910, i, 812) was used, and for the stronger alcohol a table constructed as explained later under propyl alcohol. For the weak propyl alcohols, the determination was made at 15.0/15.55°, and considered to be close enough to the conditions of Doroshevskii and Rozdestvenskii (15./15.°).

MATERIALS

Methyl Alcohol. Kahlbaum's absolute methyl alcohol was used. Its sp. g. was taken at 15.55/4.00°, and three determinations gave 0.795762, 0.795875 and 0.795877. Dittmar and Fawsett give the specific gravity of absolute methyl alcohol at 15.55/4.00°

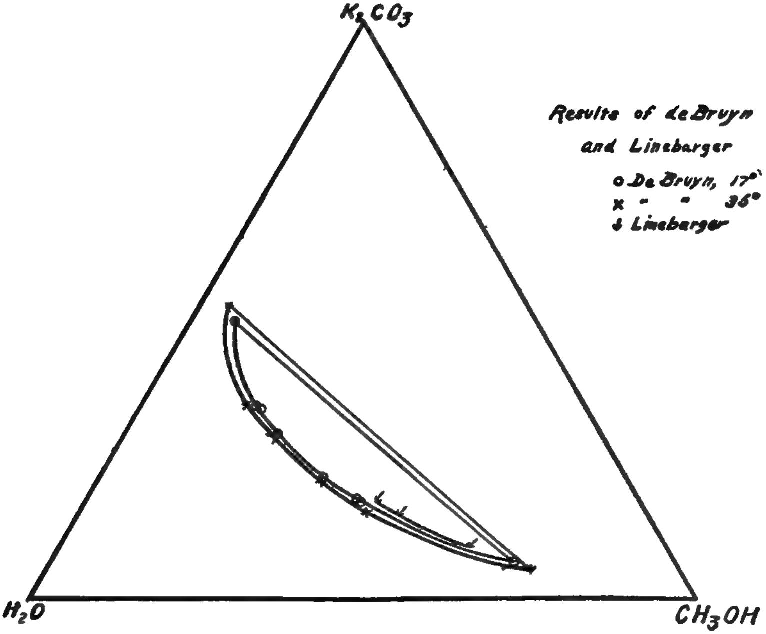


Figure 6
RESULTS OF LINEBARGER AND B. DE BRUYN

as 0.79589. The agreement was considered satisfactory, and the alcohol was figured as 100% pure.

Ethyl Alcohol.— Ordinary "95%" alcohol was digested with silver nitrate and caustic potash to remove aldehydes, and then twice distilled. Ten liters of this were prepared and carefully mixed, and stored in glass-stoppered bottles from which portions were removed to a smaller bottle for use as needed, thus preserving the main portion from contamination. From the average of four closely agreeing determinations of specific gravity, this alcohol was found to contain 91.28% by weight of absolute ethyl alcohol.

Propyl Alcohol.— For the determination of the binodal curves, Merck's normal propyl alcohol was used. It contained some water, and possibly some isopropyl alcohol. On distilling 100 cc. of it, 24 cc. came over between 91 and 94°C., and 63 cc. between 94 and 99°. Partial drying of this alcohol with anhydrous potassium

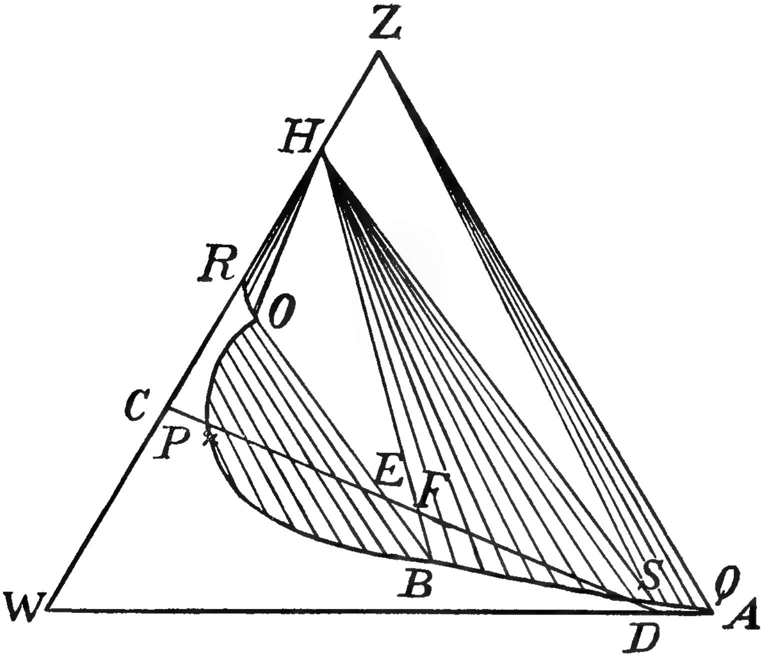
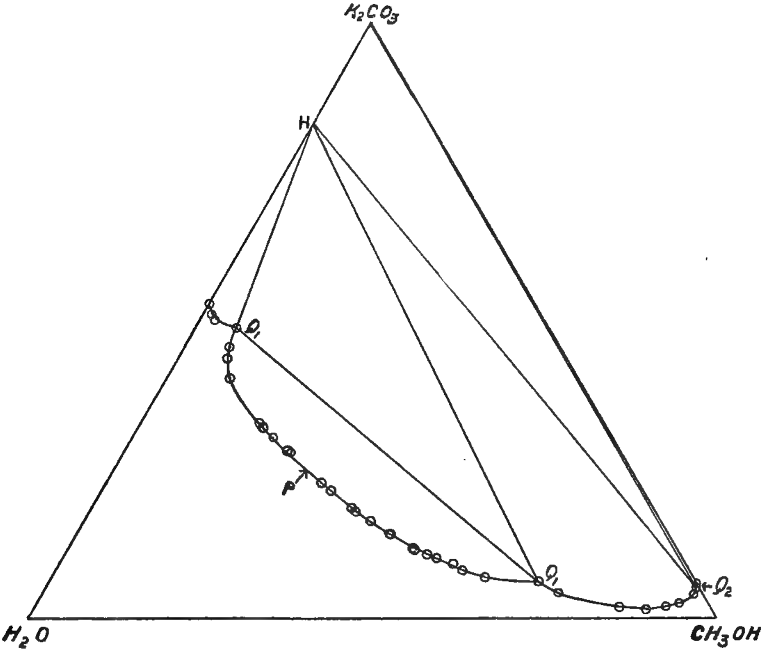


Figure 7
B. DE BRUYN'S DIAGRAM FOR THE SYSTEM: POTASSIUM CARBONATE, METHYL ALCOHOL, AND WATER

fluoride seemed to increase the proportion of the upper fraction. It is well known that the presence of water lowers the boiling point of propyl alcohol, the constant-boiling mixture boiling below 90°. The sp. g. of this alcohol at 20.0/15.55° was 0.80818. Some of the alcohol was treated with magnesium amalgam in excess, with which it reacted quite vigorously at first, and more slowly later. It stood with this for two weeks, with occasional shaking. Most of the action ceased within a few hours, but slow action was noticeable for several days. The clear liquid was filtered into a distilling flask and distilled, care being taken to protect the distillate from the air. Distillation began at 95°, and practically all of the liquid distilled over below 99°. At 15.55/15.55° two determinations of the sp. g. gave 0.80644 and 0.80647. The sp.



[Figure 8
EQUILIBRIUM IN THE SYSTEM: POTASSIUM CARBONATE, METHYL ALCOHOL, AND WATER

g. of absolute propyl alcohol is given (Linneman, Ann. *161*, 26) as 0.8066 at 15, which is in good agreement with the above. Very recently Doroshevskii and Rozdestvenskii (loc. cit.) have found a higher value, but the details of the purification of their material are not available here. They appear to have been the first ones to work out a complete table of specific gravities of mixtures of propyl alcohol and water, but as their absolute alcohol was heavier than mine, I have used their table only for very dilute solutions. Using the absolute alcohol (71 gms.) described above, in a glass-stoppered Erlenmeyer flask, I added successive amounts of distilled water, making duplicate determinations of the sp. g. of the diluted alcohol resulting from each addition. The amount of diluted alcohol remaining in the flask after each set of determinations was carefully weighed before each addition of water and the weight of the absolute alcohol in it calculated from its known strength, to correct for losses of the diluted alcohol.

The following results were obtained:

Table I

Alcohol, per cent by weight	Specific Gravity at 20.00/15.55°		
	(a)	(b)	Average
100.00	.80319	.80309	.80314
98.065	.80587	.80582	.80585
97.997	.80829	.80834	.80831
96.21	.81252	.81255	.81253
94.26	.81679	.81679	.81679
92.27	.82125	.82121	.82123
90.15	.82578	.82573	.82576
86.77	.83292	.83291	.83291

From the results obtained, the following table of specific gravities of mixtures of absolute propyl alcohol, from Merck's alcohol, was calculated:

Table II

% Alcohol	Sp. G. at 20./15.55°	% Alcoho	Sp. G. at 20./15.55°
100.00	.80314	92.00	.82185
99.00	.8058	91.00	.82395
98.00	.8083	90.00	.8261
97.00	.8108	89.00	.82825
96.00	.8130	88.00	.83035
95.00	.8153	87.00	.8325
94.00	.8175	86.00	.8346
93.00	.8197		

All strong propyl alcohol obtained in this work was determined from this table. According to it, the supply of Merck's propyl alcohol, used for most of this work, contained 98.07% by weight of the absolute alcohol.

Potassium Fluoride.— Merck's C. P. potassium fluoride was used. When freshly dissolved it was neutral to phenol phthalein, but quickly became alkaline. It contained only a trace of chloride, and appeared to be practically free from fluosilicates. No appreciable amount of sodium was shown on examination with the spectroscope, and a determination of iron and aluminum oxides

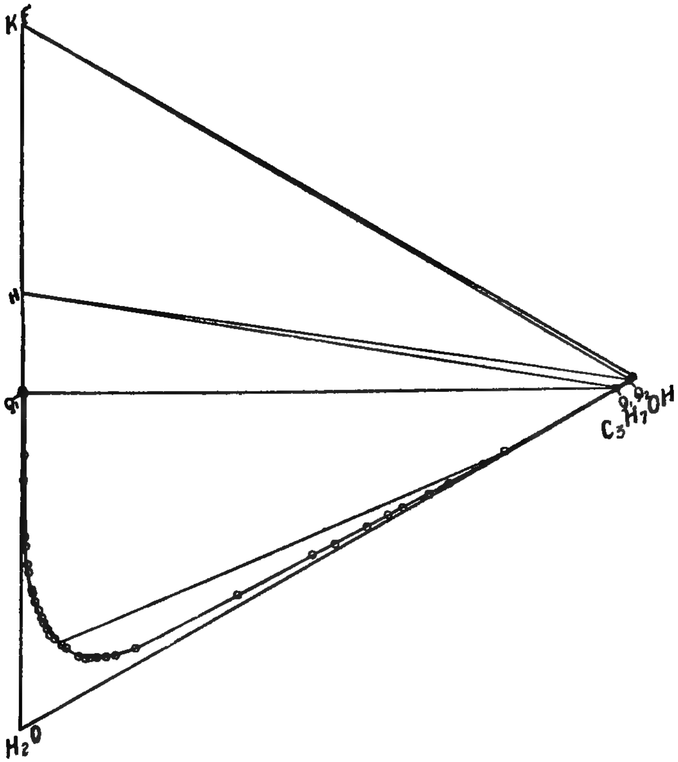


Figure 9
EQUILIBRIUM IN THE SYSTEM: POTASSIUM FLUORIDE, NORMAL PROPYL ALCOHOL, AND WATER

showed less than 0.003%. Tests for lime and magnesia gave negative results.

Potassium Carbonate.— Merck's potassium carbonate, "Highest Purity, Medicinal" was used. At first this was simply ignited and weighed, but the presence of small quantities of suspended matter, apparently oxides of iron and aluminum, was found to make it hard to get a good end point, so a quantity of the salt was dissolved in its own weight of water, filtered, and portions of this solution evaporated and ignited in platinum as needed. The solubility of the salt at room temperature was determined by evaporation and ignition of weighed quantities of the filtered saturated solution which had stood at least a week in contact with the hydrate. Duplicate determinations, two weeks apart, showed the solution to contain 53.05 and 53.07% by weight of the anhydrous salt.

Sodium Chloride.— Kahlbaum's salt, "C. P. zur Analyse" was used, the crystals being ignited for several minutes and cooled in a dessicator before weighing. Its solubility was determined as in the case of the carbonate, the saturated solution being found to contain 26.35 and 26.31% by weight of the salt. This value agrees well with those of Armstrong and Eyre (Proc. Roy. Soc., (A), *84*, 123, *79*, 566).

EQUILIBRIUM BETWEEN POTASSIUM FLUORIDE, ETHYL ALCOHOL AND WATER

This has never been studied elsewhere. Points on the binodal curve were determined at room temperature, according to the methods previously described. The effect of temperature change appears to be very slight. Careful determinations of the composition of the two layers at the quadruple point (paper, two liquid phases, solid hydrate) showed the upper layer to contain 92.69% alcohol, 6.07% water and 1.23% potassium fluoride by weight, while the lower layer contained only 0.67% alcohol by weight.

Two sets of conjugate solutions were analysed, to locate tie-lines and get an approximate idea of the position of the plait-point. They are shown in Figure 2, which presents graphically the equilibrium in the system. (For all the analytical data, see Research Bull. 1 of the University of Minnesota, which will soon be issued and may be obtained by applying to the President of the University.)

A good many experiments were performed in the attempt to locate accurately the position of the second quadruple point (vapor, liquid, anhydrous salt, hydrate), which will determine the extent to which the fluoride will dehydrate alcohol. Preliminary experiments showed that it was very easy to obtain alcohol containing about 96% by weight of absolute alcohol, but it appeared that the process of dehydration by repeated treatment with the anhydrous salt at boiling temperature, cooling, and decanting the solution did not raise the purity rapidly above

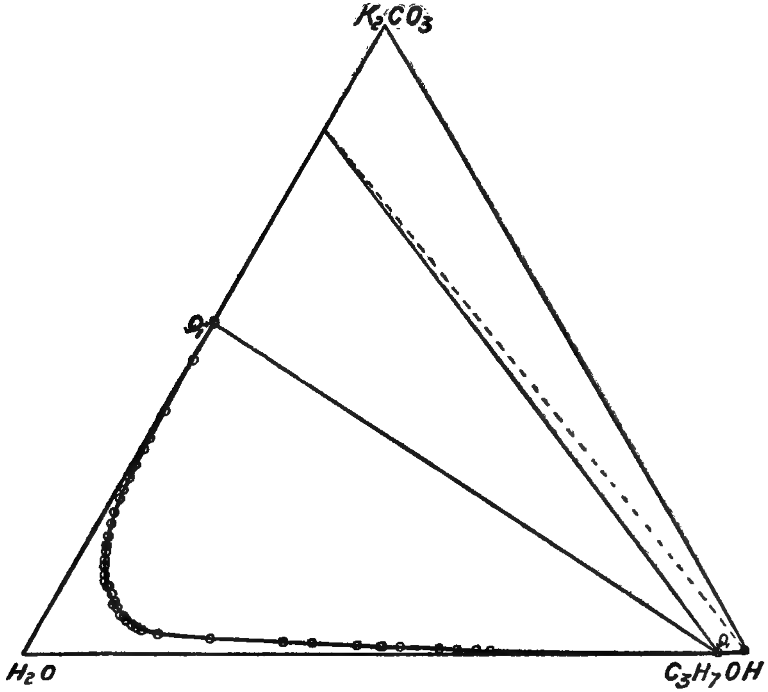


Figure 10

EQUILIBRIUM IN THE SYSTEM: POTASSIUM CARBONATE, NORMAL PROPYL ALOCHOL, AND WATER

this point. By long standing at room temperature, however, a sample of alcohol was obtained which gave a distillate containing 97.37% alcohol by weight. As the result of repeated treatment, (refluxing, cooling to –7°, decantation) with the anhydrous fluoride, an alcohol was obtained which after standing ten days at room temperature with excess of the hydrated salt, contained 1.52% by weight of anhydrous potassium fluoride, and gave a distillate containing 97.50% alcohol. Several experiments in grinding the anhydrous salt in a ball-mill with alcohol gave solutions containing this same amount of alcohol, or slightly less. This appears to be the solution at the quadruple point, and its composition was calculated to be: alcohol 96.05%, water 2.43%, potassium fluoride 1.52%.

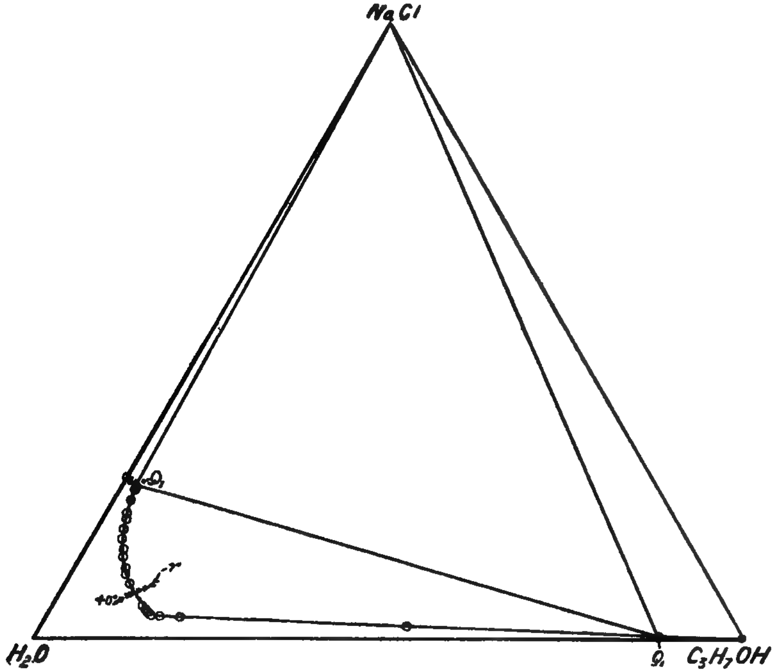


Figure 11
EQUILIBRIUM IN THE SYSTEM: SODIUM CHLORIDE, NORMAL PROPYL ALCOHOL, AND WATER

The solubility of the anhydrous salt in absolute (99.58%) alcohol was determined, the saturated solution being found to contain 4.57% by weight of the salt. It is to be noticed that although the saturated aqueous solution of the salt contains 48% of it by weight, (Mylius and Funk, Ber., 1897, *30*, 1716) yet the addition of water to the solution in absolute alcohol decreases the solubility of the salt in it to a marked extent: from 4.79 gm. per 100 gm. solvent in 99.6% alcohol to 1.54 gm. per 100 gm. solvent in 97.5% alcohol. A similar decrease in solubility with the first increase in water content of the alcohol appears also in the case of the fluoride with propyl alcohol, and the carbonate with all the other alcohols, but not with sodium chloride and propyl alcohol. It is interesting to note that the solu-

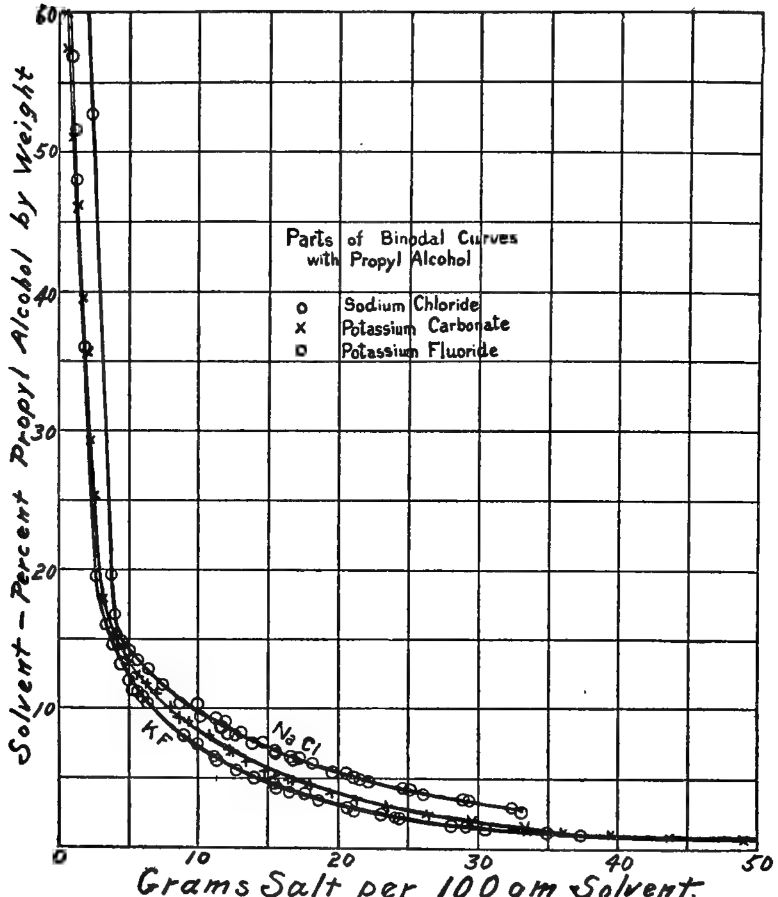


Figure 12
EQUILIBRIA IN SYSTEMS: POTASSIUM FLUORIDE, NORMAL PROPYL ALCOHOL, WATER, POTASSIUM CARBONATE, NORMAL PROPYL ALCOHOL, WATER, AND SODIUM CHLORIDE, NORMAL PROPYL ALCOHOL, WATER

bility of the fluoride in absolute ethyl alcohol is about the same as in 60% alcohol.

In general, the solubility of a salt in aqueous alcohol decreases as the concentration of the alcohol increases. (Gerardin, Ann.

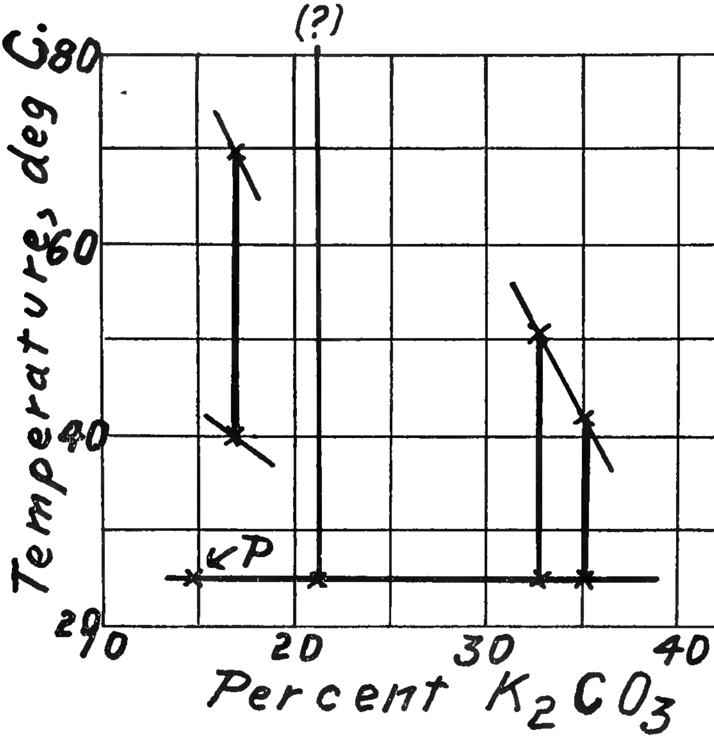


Figure 13
CRITICAL SOLUTION TEMPERATURES IN SYSTEM: POTASSIUM CARBONATE ETHYL ALCOHOL, WATER

Chim. Phys., (4), *5*, 129.) But L. de Bruyn has shown (Z. Phys. Chem. 1892, *10*, 782) that in absolute methyl alcohol the hydrated salts $MgSO_4.7H_2O$, $ZnSO_4.7H_2O$, $CoSO_4.7H_2O$, $NiSO_4.7H_2O$, $FeSO_4.7H_2O$, $NiSO_4.6H_2O$ and $CuSO_4.5H_2O$, were readily soluble, but were quickly precipitated again as the lower hydrates, (especially on adding a drop of water) or as lower hydrates in which part of the water of crystallization was replaced by alcohol. In 93% alcohol they were only slightly soluble, and less so in the more dilute alcohols down to 50%. He states that ethyl alcohol shows a similar behavior, but that it is less marked. Bödker (Z. Phys. Chem. 1897, *22*, 505) found that anhydrous cobalt and

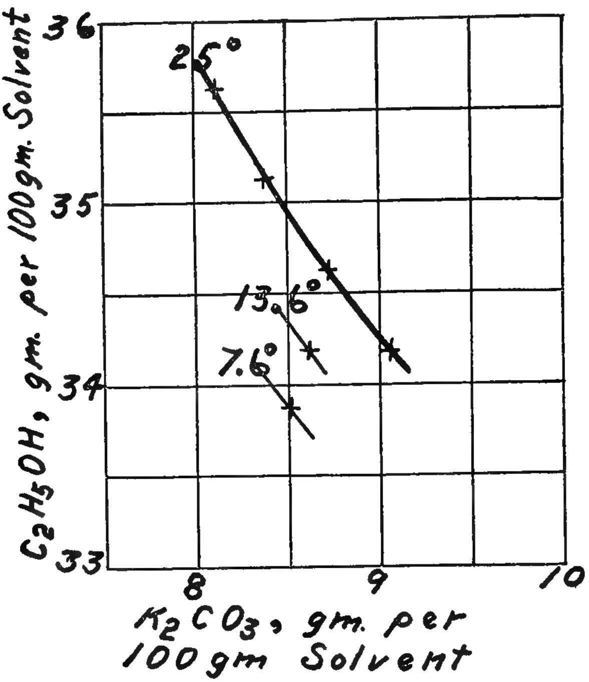


Figure 14
ISOTHERMS IN THE SYSTEM: POTASSIUM CARBONATE, ETHYL ALCOHOL AND WATER

copper chlorides were very soluble in absolute alcohol but that the addition of water caused the immediate precipitation of the hydrate. The results here shown with potassium carbonate and fluoride seem to be somewhat similar in principle, though of an entirely different class of salt, as far as the degree of hydration is concerned. But dilution of the solution of the anhydrous fluoride with water failed to produce precipitation of the hydrate, probably due to supersaturation phenomena, which were frequently noticed with alcoholic solutions of the hydrate which had been prepared at high temperatures and cooled out of contact with the solid phase. It is particularly noticeable that sodium chloride, which does not form a crystalline hydrate at ordinary temperatures,was least soluble in the strongest propyl alcohol.

Beside the well-known methods for the determination of alcohol by the specific gravity of a solution, and by its boiling point (Ebullioscope), many others have been studied in the attempt to find advantageous methods. Oxidation with either bichromate or permanganate has been studied by many.

The refractive index of mixtures of alcohol and water offers another method which has been well studied, and appears to be of practical value in some cases.

Indirect methods, depending on the change in specific gravity of a liquor after removing alcohol by evaporation and making up again to the same volume, have been discussed by a number of authors to determine the alcoholic content, (Duclaux, Ann. chim. phys., (5), *2*, 233; Gossart, Compt. rend., *113*, 537) as has also the lowering of the freezing point, (Gaunt, Z, Anal. Chem., 1905, *44*, 106, the solubility of cinchonine in chloroform containing alcohol, (Oudemans, Ann., *166*, 78, J. Chem. Soc., 1873, *26*, 533) the Pasteur drop reaction (Klocker, Centr. Bakt. Parasitenk., II Abt., *31*, 108, C. A., 1912, *6*, 136) and the color produced by cobalt salts in the presence of a sulphocyanide. (T. T. Monell, Chem. Zentr., 1877, 24.)

(Thresh, Chem. News, *38*, 251; Röse, Z. angew. Chem. *1*, 31; Bourcart, Bull. Soc. Ind. Mulhouse, *59*, 558, J. Chem. Soc., 1890, *58*, 1030; Frankland and Frew, J. Chem. Soc., 1891, *59*, 93; Grünhut, Chem. Zeit., *15*, 847, J. Chem. Soc., 1892, *62*, 1031; Benedikt and Neudörfer, Chem. Zeit., *16*, 77; Kuriloff, Ber. 1897, *30*, 741; Benedict and Norris, J. Am. Chem. Soc., 1898, 20, 293; Lassar-Cohn, Z. anal. Chem., 1899, *38*, 251; Argenson Bull. Soc. Chim., 1902, (3) *27*, 1000; Pozzi-Escot, Ann. chim. anal., 1902, *7*, 11; 1904. *9*, 126; Nicloux, Ann. chim. anal., 1904, *9*, 214; Martin, Rev. intern. Falsif., 1904, *17*, 48, J. Chem. Soc., 1904, *86*, ii, 520; Janak, Oesterr. Chem. Ztg., (2), *14*, 17, C. A., 1911, *5*, 2761.)

(Riegler, Z. anal. Chem., 1896, *35*, 27; Ling and Pope, J. Fed. Inst. Brewing, 1901, *7*, 170, J. Chem. Soc., 1901, *80*, ii, 628; Leach and Lythgoe, J. Am. Chem. Soc., 1905, *27*, 964; Ackermann and Steinmann, Zeit. ges. Brauw., *20*, 259, Chem. Zentr., 1905, ii, 1672; Ackermann, Ann. chim. anal., 1905, *10*, 171; Kamenetzky, Chem. Ztg., *31*, 257; Doroshevskii and Dvorzhanchiik, J. Russ. Phys. Chem. Soc., *40*, 101, *41*, 849, C. A., 1908, *2*, 2181, *4*, 135, 1403; Race, J. Soc. Chem. Ind., *27*, 547; Andrews, J. Am. Chem. Soc., 1908, *30*, 353; Frank-Kamenetsky, Z. angew. Chem., *23*, 293; Sidersky, Bull. assoc. sucr. dist., *27*, 1168, C. A., 1910, *4*, 2759, Ann. chim. anal., *16*, 142, C. A., 1911, *5*, 2143.)

(Blunt, Analyst, 1891, 221; Richmond, J. Fed. Inst. Brewing, 1896, *2*, 529, J. Chem. Soc., 1897, *72*, 193; Leonard and Smith, Analyst, *22*, 225; Pharm, Zentr., *49*, 971; Gunzel, Z. Nahr. Genussm., *18*, 206, C. A., 1909, *3*, 2717; Bonis, Ann. fals., *4*, 276, C. A., 1911, *5*, 3492.)

More closely allied to the method which I have to propose are the methods of Hagar (Chem. Zentr., 1888, 1512) and Böttger (Chem. Zentr., 1872, 742) who shake out the alcohol from essences with glycerine, and measure the increase of volume; Curtis, (J. Physic. Chem., 1898, *2*, 371) who titrates alcohol of 85% or over with toluene; and Bohlig (Z. anal. Chem., *25*, 19) who salts out the alcohol with potassium carbonate, and measures the volume of the layer obtained, standardizing the apparatus with known weights of absolute alcohol.

Methods involving the critical temperature of solution of alcohol-water mixtures with other liquids have also been worked out. The method of Crismer (Bull. assoc. belge. des Chemistes, *16*, 83, Chem. Zentr., 1902, ii, 3) using kerosene, is said to be very accurate, but is only applicable to very strong alcohol, while the method of Buboux and Dutoit, (Ann. Chim. Anal., *13*, 4, see also Duperthuis and Philippe, Mitt. Lebensm. Hyg., *1*, 188, C. A., 1911, *5*, 3118) using a mixture of aniline and alcohol, is only suitable for mixtures containing from 8 to 12% alcohol. An apparatus for the determination of alcohol, based on the solubility of ether in alcohol of various strengths (*i. e.*, the binodal curve in the system, alcohol, ether, water) has been patented and described. As specially pure ether and 98% alcohol are used to make the determination, it would hardly seem to be an easy and convenient method, and the accuracy may well be doubted.

If the binodal curve in the system containing a salt and aqueous alcohol has a small enough temperature coefficient, and can be determined with sufficient accuracy, it ought to be possible to add to a liquid of unknown alcoholic content enough of the salt to cause the solution to separate into two layers, and then, by the cautious addition of water, get the solution to be just homogeneous again. Now, if the weights used are known, the composition of the original alcohol can be found, since the composition of the solution which we have made homogeneous is represented by that point on the binodal curve which expresses the relation of the amount of salt to the whole solution or to the amount of solvent

(H. Kapeller, D. R. P., 213, 127, Oesterr. ung. Z. Zuckerind. Landw., *38*, 817, C. A., 1910, *4*, 232, 2348; Sidersky, Ann. chim. anal. appl., *15*, 105, Bull. assoc. sucr. dist., *27*, 562, C. A., 1910, *4*, 1793, 1648.)

present. Since there can only be one solution which contains this proportion of salt, on the line separating the homogeneous from the inhomogeneous solutions, this fixes the composition of the final solution definitely, and the weight of alcohol present can easily be computed.

While the method of Schreinemakers for representing such equilibria, as described on a previous page, is convenient and useful in many ways, it is not suitable for determination of the slope of the curve for analytical purposes, as triangular co-ordinates are inconvenient and the most important part of the curve comes at a point where the figure is very much compressed. For this reason, the results obtained have been calculated also on the basis of the weight of each component present in that quantity of the solution which contains 100 gm. of the solvent. Since the sum of the weights of water and alcohol here will be 100, this relation can be plotted in rectangular co-ordinates, the composition of the solvent being shown on one axis, and the amount of salt per 100 gm. solvent on the other. Such a curve also represents directly the solubility of the salt in alcohol of all strengths. In Figure 3 such curves have been plotted for both potassium fluoride and potassium carbonate, and show well the difference between these salts in their behavior toward alcohol. It is noticeable that at concentrations above 30 grams of salt per 100 grams of solvent the curves are nearly identical, although above 50 grams per 100 gm. solvent, the solubility of the alcohol in the solution of the carbonate is a little less than in that of the fluoride. It will be noted that the results for the fluoride form a smooth curve with which the individual results are in much better accord than is the case with the carbonate. The end point seemed to be more definite in the first case, and apparently the effect of temperature is less. For this reason the table recommended has been calculated on the basis of the fluoride curve, and is given in Table 3.

TABLE III

Determination of Alcohol by means of the Binodal Curve of the Ternary System: Water, Alcohol, Potassium Fluoride.

Gm. per 100 gm. solvent		
KF	C_2H_5OH	d
60	2.82	.10
59	2.92	.10
58	3.02	.10
57	3.13	.11
56	3.24	.11
55	3.36	.12
54	3.48	.12
53	3.61	.13
52	3.75	.14
51	3.90	.15
50	4.06	.16
49	4.23	.17
48	4.41	.18
47	4.60	.19
46	4.80	.20
45	5.01	.21
44	5.24	.23
43	5.48	.24
42	5.74	.26
41	6.02	.28
40	6.32	.30
39	6.65	.33
38	7.01	.36
37	7.40	.39
36	7.83	.43
35	8.30	.47
34	8.81	.51
33	9.37	.56
32	9.98	.61
31	10.64	.66
30	11.36	.72
29	12.14	.78
28	12.99	.85
27	13.92	.93
26	14.94	1.02
25	16.07	1.13
24	17.33	1.26
23	18.75	1.42
22	20.26	1.50
21	21.80	1.54
20	23.40	1.60
19	25.10	1.70
18	26.90	1.80
17	28.8	1.9
16	30.8	2.0
15	32.9	2.1
14	35.0	2.1
13	37.2	2.2
12	39.4	2.2
11	41.7	2.3
10	44.0	2.3
9	46.4	2.4
8	49.0	2.6
7	51.9	2.9
6	55.1	3.2
5	58.7	3.6
4	62.8	4.1
3	67.5	4.7
2	78.6	11.1

To determine alcohol in an alcoholic liquid with this table, a stoppered flask is weighed, some freshly ignited potassium fluoride is weighed into it, a weighed amount of alcoholic liquid added, and the fluoride dissolved. From the probable alcoholic content of the liquid used, the proportions of liquid and salt are so chosen that there will be salt enough to cause the liquid to separate into two phases, *i.e.*, if a whiskey supposed to contain from 40-50% alcohol is being tested, the salt should be in the proportion of at least 12 gm. per 100 gm. whiskey, and then a separation will take place if the whiskey contained more than 39.4% alcohol, as indicated by Table 3. If the solution is now brought to approximately 25°, and water added cautiously, with frequent shaking, until the solution just becomes homogeneous, and the whole weighed again, the proportion of the salt present to the total weight solvent (whiskey plus water) gives by reference to the table, the per cent of alcohol in such total weight of solvent, hence the weight of alcohol in the sample. For rapid work, if 100 gm. of the liquid under examination be taken, and all weights carried only to the nearest tenth of a gram, reasonably accurate results could be secured in a very few minutes. If extreme accuracy is not desired, and care is taken in the preservation of the fluoride, it might be used without previous drying, making correction for water held as determined by one or two tests.

It is obvious that the method would not be very accurate in the presence of large quantities of dissolved solids, as in the case of a beer. But in the determination of alcohol in liquids where solids are absent, the good agreement of the data plotted in figure 3 with the smooth curve indicates that it would be satisfactorily accurate. One determination carried out on alcohol which had a sp. g. of 0.95223 (33.13% by weight) gave 33.18%. Heating the solution to 35° caused the solution to cloud a little, and when the titration was completed at that temperature, 33.53% of alcohol was found. The temperature coefficient for such a solution was evidently negligible within the range to which it would be easy to confine the temperature of the determination.

Since methyl alcohol is not precipitated by potassium fluoride, it was thought interesting to see what effect the presence of a certain amount of methyl alcohol would have on the determination of ethyl alcohol by this method. By weighing out some of the ethyl alcohol previously used, and mixing it with a weighed amount of absolute methyl alcohol, a solution was made containing 85.55%

ethyl alcohol, 6.72% methyl alcohol and 8.17% water by weight. The weight of methyl alcohol was thus 7.33% of the weight of absolute ethyl alcohol present. A series of determinations were made with this mixture and potassium fluoride, and the results are plotted in Figure 4. In plotting these, the quantity (d) chosen to be plotted against the concentration of the salt was the amount by which the per cent of ethyl alcohol in the solution was changed, *i.e.*, the error in the determination of the ethyl alcohol caused by the presence of 7.33% of its weight of methyl alcohol. A negative value indicates that too little alcohol would be found, on account of the increase in the solubility of the ethyl alcohol in the potassium fluoride solution, caused by the presence of the methyl alcohol, while a positive value indicates that too high a result would be found, the methyl alcohol here decreasing the solubility of the ethyl alcohol. It is surprising to note that in concentrated solutions there appears first a negative effect, over a wide range, and the methyl alcohol in the mixture acts as a solvent for the ethyl alcohol, then conditions appear to be reversed, although the results are not very concordant, then between 25 and 15 gm. salt per 100 gm. solvent, the determination is correct, within the limits of experimental error, and from this point down, the solubility of the ethyl alcohol is decreased by the methyl alcohol to a constantly increasing extent. This is a phenomenon worthy of further investigation, but it appears probable that within certain concentrations, ethyl alcohol can be satisfactorily determined in the presence of methyl alcohol by this method.

SYSTEM POTASSIUM CARBONATE ETHYL ALCOHOL WATER

Potassium carbonate is a salt which is much more often found in the laboratory than potassium fluoride, and therefore would be more convenient for analytical purposes. This system was therefore studied, and the position of the binodal curve determined. This salt was the first ever noted as having the power to salt out alcohol, as it is known that Raymond Lully (1235-1355) used and described it for that purpose. The composition of the solutions formed was first studied by Lescoeur (Bull. Soc. Chim., 1897, (3) *17*, 18), who determined the composition of the upper layer at the quadruple point: vapor, two liquids, solid.

A few determinations of points on the binodal curve were made by Linebarger (Am. Chem. J., 1892, *14*, 380) but the method used could not give accurate results, and the points determined all lie within a small part of the curve.

B. de Bruyn (Z. Phys. Chem., 1900, *32*, 63) determined the composition of the two solutions in equilibrium at the quadruple point. According to his own statements the accuracy of his alcohol determinations leaves much to be desired, duplicates differing by nearly two per cent being recorded. His determinations nearest room temperature are those at 17 and 35°. Bell (J. Phys. Chem., *9*, 531) has determined the composition of nine solutions lying on the binodal curve, and recently Cuno (Ber. Physik. Ges., *5*, 735; Ann. Physik, *25*, 346) determined the composition of eight sets of conjugate solutions. He states (Ann. Physik, *28*, 663) that his results agree fairly well with those of Bell, but plotting them together shows that his curve lies above that of Bell for its whole length, the difference in alcohol content between solutions of the same salt contents in the two curves being often nearly a per cent. His results are the most complete yet published, but his method of determination of the alcohol present (by the conductivity of the solution) might be open to question as the foundation of another analytical method. His determinations do not reach as far as the quadruple point.

As previously stated, some difficulty was experienced at times in obtaining good end points with this salt, so a larger number of determinations were made than in the case of the fluoride. The complete curve for the system is shown in Figure 5 for the first time. Although the formula of the hydrate of this salt has been in dispute, it was considered that the recent work of de Forcrand (Compt. rend., *148*, 1731) and Foote and Sholes (J. Am. Chem. Soc., 1911, *33*, 1309) identify the sesquihydrate as the one stable at ordinary temperatures and so this has been plotted in the figure. A number of conjugate solutions were analysed, to locate tie-lines, some of which have been plotted in the figure. The quadruple point where two liquid phases exist was determined; the upper solution was found to be alcohol, 90.56%, water 9.34%, potassium carbonate, 0.09%, and the lower one alcohol 0.28%, water 46.53%, carbonate 53.09%. The addition

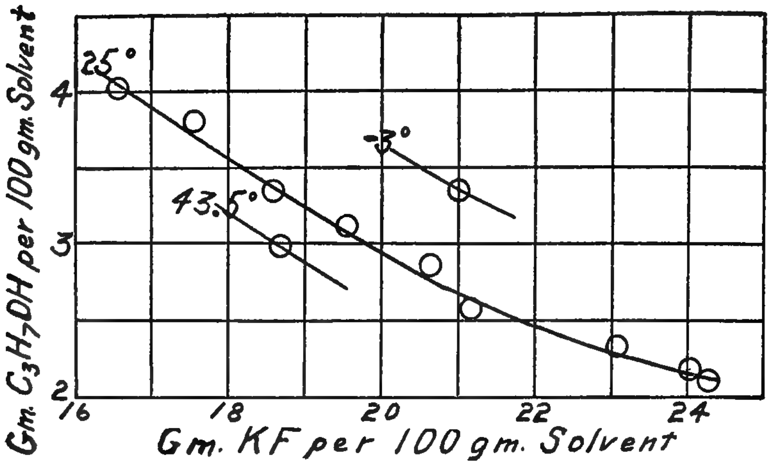


Figure 15
ISOTHERMS IN THE SYSTEM: POTASSIUM FLUORIDE, NORMAL PROPYL ALCOHOL, WATER

of the alcohol has thus not appreciably decreased the solubility of the salt in the water.

Saturated solutions of the salt in 97.5% and 99.6% alcohol were analyzed, and found to contain 0.054% and 1.64% of carbonate respectively. The same increase in the solubility of the salt in the anhydrous alcohol is to be noted here as in the case of the fluoride. As the mixture of anhydrous salt and hydrate is in equilibrium with 99.6% alcohol (Foote and Sholes, loc. cit.) this locates the other quadruple point.

In Table 4 will be found the approximate values corrected from the curve in Figure 3 over the range in which the curve is quite definitely determined. These values may be used for the determination of alcohol, in the same manner as those in Table 3, using dried carbonate, free from insoluble impurities, but the use of the fluoride appears more likely to give accurate results.

TABLE IV

Gm. per 100 gm. solvent			Gm. per 100 gm. solvent		
K_2CO_3	C_2H_5OH	d	K_2CO_3	C_2H_5OH	d
45	5.0	.2			
44	5.2	.2	21	18.9	1.1
43	5.4	.2	20	20.0	1.1
42	5.7	.3	19	21.1	1.1
41	6.0	.3	18	22.3	1.2
40	6.3	.3	17	23.5	1.2
39	6.6	.3	16	24.7	1.2
38	7.0	.4	15	26.0	1.3
37	7.4	.4	14	27.2	1.2
36	7.8	.4	13	28.5	1.3
35	8.3	.5	12	29.8	1.3
34	8.8	.5	11	31.1	1.3
33	9.3	.5	10	32.5	1.4
32	9.9	.6	9	34.0	1.5
31	10.5	.6	8	35.7	1.7
30	11.2	.7	7	37.5	1.8
29	11.8	.6	6	39.6	2.1
28	12.5	.7	5	42.0	2.4
27	13.2	.8	4	44.7	2.7
26	14.0	.8	3	48.3	3.6
25	14.9	.9	2.5	50.3	2.0
24	15.8	.9	2	52.6	2.6
23	16.8	1.0			
22	17.8	1.0			

In Figure 3 the curves for both the fluoride and the carbonate are plotted in rectangular co-ordinates, and the quadruple-point tie-lines drawn. The determinations marked with a circle having a diameter drawn in are in the carbonate system, and it will be noticed that a number of them lie quite a distance from the line. The cause of this error was the uncertainty in the end point, due to suspended matter, which obscures the disappearance of the emulsion. If the carbonate is to be used for the analytical method, it must be freed from such matter by solution, filtration and evaporation. All weights above and elsewhere refer to the anhydrous salt. Where a large number of determinations were to be made, a strong solution might be prepared and standardized, and weighed portions used. A crystal or two of solid phenol phthalein is the best indicator.

The curve and table may be considered to be approximately correct for room temperature. Some experiments designed to show the influence of temperature will be discussed in the latter part of the paper.

SYSTEM POTASSIUM CARBONATE METHYL ALCOHOL, WATER

This system was first investigated by Linebarger (Am. Chem. J., 1892, *14*, 380), who made three determinations of points on the binodal curve. As shown in Figure 6, his results are evidently far from accurate, as they lie on a curve which must be true for temperatures near zero. De Bruyn (Z. Phys. Chem., 1900, *32*, 63) determined the position of the quadruple point at 17 and 35°, three other tie-lines on the binodal curve at the first temperature and two at the second. He recalculated Linebarger's results and showed their inaccuracy, and gave a general ("schematisch") curve to show the form of the isotherm. This is reproduced in Figure 7, to compare with the diagram of the isotherm which I have determined at room temperature (Figure 8) and the plot of the actual results obtained by him and by Linebarger (Figure 6). The only other work which appears to have been done on this system is that of Wrewsky (J. Russ. Phys. Chem. Soc., 1900, *32*, 593, J. Chem. Soc., 1901, *80*, ii, 56) who showed that the vapor pressure of the system increased with the proportion of the salt present. He showed that, as was to be expected, the two layers formed in the system had the same vapor pressure, the partial pressure of the water being lowered and that of the alcohol raised by the presence of the salt. He also studied the effect of temperature on the vapor pressure of the system.

As potassium carbonate appears to be the only salt which is capable of precipitating methyl alcohol at ordinary temperatures, this system was studied to see how closely it resembled the others. The binodal curve was determined, as in the other cases. Determinations of the composition of the two layers in equilibrium at the quadruple point were made by the same methods as in the other cases. The upper layer contained: methyl alcohol, 75.85%, water 17.83% and potassium carbonate 6.32%. The lower layer contained: methyl alcohol 6.10%, water 44.85% and potassium carbonate 49.05%. Several determinations of the solubility of the carbonate in stronger solutions of methyl alcohol were made. Samples of methyl alcohol containing 86.7, 90.5, 96.2 and 100% by weight of the alcohol gave solutions which contained respectively 2.05, 1.56, 2.72 and 5.64% by weight of potassium carbonate. Two other solutions, obtained in the process of locating the upper quadruple point (vapor, liquid, anhydrous salt, hydrate) were analysed and found to contain (a) alcohol 90.96%, water 7.06%, carbonate 1.98% and (b) alcohol 94.74%, water 0.87%, carbonate 4.39% by weight, respectively.

The determination of this upper quadruple point, by dehydration of 90% methyl alcohol with the ignited and pulverized carbonate, showed that at that point the solvent (or distillate if the solution be distilled) contains 99.35% alcohol by weight, while the solution as a whole contains alcohol 94.14%, water 0.33% and potassium carbonate 5.53% by weight.

Since the lower layer at the quadruple point (vapor, two-liquid layers, hydrate) contained only 49.05% carbonate, while the saturated aqueous solution contained 53.06%, attempts were made to get points along the line joining these two points. Two determinations were made by adding known quantities of the alcohol to strong aqueous carbonate solutions, and then water in small quantities until the salt precipitated had just redissolved. These and all the other determinations have been plotted and are shown in Figure 8.

SYSTEM POTASSIUM FLUORIDE, PROPYL ALCOHOL, WATER

The binodal curve was determined at room temperature as in the other systems, and the results are plotted in Figures 9 and 12. Experiments showed that the influence of temperature on the position of the binodal curve was quite marked in all cases in which propyl alcohol was one of the components of the system. Some observations on the effect of such changes at several points in the curve were therefore made, and are discussed under a later heading. (Temperature coefficients and critical solution Temperatures.) Determinations of the composition of the two liquid layers in equilibrium at the quadruple point were made as in the other systems, and the lower solution was found to contain 47.62% potassium fluoride and 0.039% propyl alcohol by weight, while the upper solution contained 96.78% propyl alcohol and 0.17% potassium fluoride. A determination of the solubility of potassium fluoride in 99.6% propyl alcohol showed that the saturated solution at room temperatures contained 0.34% of the anhydrous fluoride. One tie-line was investigated, the upper solution by analysis containing 78.91% of the alcohol and 0.31% fluoride by weight, while the lower solution contained 9.67% fluoride by weight. This tie-line has been drawn on Figure 9.

A determination of the composition of the liquid layer at the second quadruple point (vapor, liquid, anhydrous salt, hydrate) showed it to be: propyl alcohol, 98.44%, potassium fluoride, 0.28%, water, 1.28% by weight.

SYSTEM POTASSIUM CARBONATE, PROPYL ALCOHOL, WATER

The determinations of points on the binodal curve were made as in the other systems, and are plotted in Figures 10 and 12. The temperature of the solution was frequently tested during each series of determinations, and kept between 22 and 26°. Some determinations of the effect of change of temperature on the position of the binodal curve were made, and are discussed later. Duplicate determinations of the amount of carbonate in the lower solution at the quadruple point gave 53.05 and 52.89%, or practically the same as in saturated solutions of the carbonate at room temperatures (53.06%). A determination of the propyl alcohol content, in the distillate from about 300 gm. of the solution, showed this to be only 0.02% by weight. The upper solution contained 0.017% by weight of the carbonate, and 95.83% of propyl alcohol. It will be noted that as in the case of the quadruple point determinations with ethyl alcohol, the upper layer in the system containing potassium carbonate is a weaker alcohol than in the system containing the fluoride. This indicates as previously shown, that the saturated solution of the fluoride has a lower vapor tension than that of the carbonate. Determination of the solubility of the anhydrous carbonate in 99.6% propyl alcohol showed that the saturated solution under ordinary conditions contained 0.031% of the salt. The fluoride is therefore ten times as soluble as the carbonate in absolute propyl alcohol at their respective quadruple points. The other quadruple point, (vapor, liquid, anhydrous salt, hydrate) was not determined, as from the known vapor pressure of the hydrate of the salt, this point would undoubtedly lie within a few tenths of a per cent of 100% alcohol, and unless a quantity of specially pure alcohol was available, so that the actual gravity of the absolutely pure alcohol, carefully dried, could be obtained, it would be a waste of time to attempt the determination of this point.

SYSTEM SODIUM CHLORIDE, PROPYL ALCOHOL, WATER

As an example of a salt only moderately soluble in water, not capable of crystallizing with water of crystallization under ordinary conditions, and possessing obviously a low affinity for water, sodium chloride was chosen as the precipitant to compare with potassium carbonate and fluoride. The binodal curve was determined as in the other systems, and the determinations are plotted in Figures 11 and 12. The first three series of determinations were made at room temperature, but without special care to control the temperature. In the last series, containing the solutions high in alcohol, where it would exert an influence that might be very disturbing, the temperature was taken frequently, and kept between 23 and 25°. The fact that those determinations in this series which fall within the limits of concentration covered by the other two series check well with them would indicate that the temperature in these series was not seriously different from that assumed (23 to 26°). As we do not have in the case of sodium chloride the relatively large heat of dilution which is found with the other two salts, the only factor tending to raise the temperature unduly was the heat of the hands, and the effect seems to have been negligible.

Determinations of the effect of temperature on the equilibrium showed that this is a much greater factor than in the case of the other two salts. This will be discussed in detail under the next head.

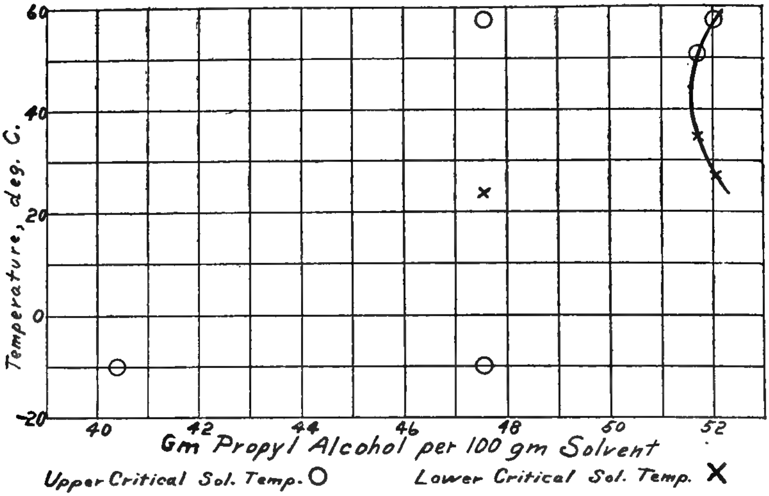


Figure 16

UPPER AND LOWER CRITICAL SOLUTION TEMPERATURES IN THE SYSTEM: POTASSIUM CARBONATE, NORMAL PROPYL ALCOHOL, WATER

There is only one quadruple point in this system, as the salt does not form a crystalline hydrate at this temperature. The upper layer at this quadruple point contains 87.70% propyl alcohol and 0.55% salt by weight, while the lower layer contains 2.47% propyl alcohol and 24.90% salt. The saturated aqueous salt solution contained 26.33% of salt. The precipitation of salt from a saturated solution by addition of propyl alcohol has been studied by Armstrong and Eyre (Proc. Roy. Soc., (A) *84*, 123) and their determinations have been plotted in Figure 11 to give the line joining the saturated salt solution with the lower layer at the quadruple point.

Parts of the binodal curves for the three systems involving propyl alcohol have been drawn in rectangular co-ordinates in Figure 12. It will be noticed that the curves are in general parallel, but the curve for the carbonate lies above that for the fluoride at concentrations from three to forty grams of salt per 100 gm. solvent, and below it for concentrations outside these limits. This is exactly the reverse of the condition of things shown in

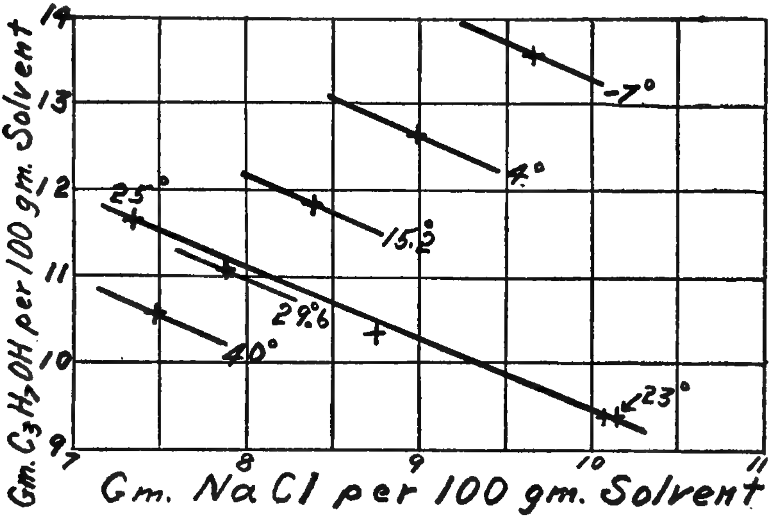


Figure 17
ISOTHERMS IN THE SYSTEM: SODIUM CHLORIDE, NORMAL PROPYL ALCOHOL, WATER

the systems involving ethyl alcohol (Figure 3) and would indicate that the relative salting-out power of different salts depends to a certain extent on the individual substance treated, and not, as some authors have stated, entirely upon the anion and cathion of the salt. The fact that sodium chloride, which is here shown to be nearly as good a salting-out agent as potassium carbonate for propyl alcohol, does not salt out ethyl alcohol at all, although it is relatively insoluble in strong alcohol, is another indication that we cannot reason from a few isolated cases to form a general theory of the salting-out process.

TEMPERATURE COEFFICIENTS AND CRITICAL SOLUTION TEMPERATURES

By the critical solution temperature of a mixture we understand that temperature at which the solution just becomes homogeneous. We may then distinguish between upper and lower critical solution temperatures, according as warming or cooling of the solution at that temperature produces homogeneity. For tenary systems a general theory of the critical solution temperatures has recently been given by Timmermans. (Z. Phys. Chem., *58*, 129.) He considers that all liquid pairs have in reality both an upper and a lower critical solution temperature, although neither or only one of them may be experimentally realizable. For the case of miscible liquids, such as those studied in this work, he assumes that the upper critical temperature lies below the lower critical temperature, and that the addition of a salt has the effect of either raising the upper critical temperature or lowering the lower critical temperature. If this effect is great enough, the upper critical temperature may come to its normal position above the lower critical temperature, and we have the possibility of the formation of two layers (salting-out) between these two temperatures.

The theoretical requirement that the salt be insoluble in one of the pair of liquids and quite soluble in the other in order to produce separation, does not seem to be rigidly necessary. It has been shown in this work that while potassium carbonate salts out methyl alcohol, it dissolves to the extent of over 6 gms. per 100 gms. solvent in the absolute alcohol, and in some of the other cases the solubillty of the salt in the alcohol is not small. But in all cases the solubility in alcohol containing some water is fairly small; it appears then that the theoretical statement should refer only to the solubility of the salt in mixtures containing a large excess of either component, and not to the pure liquids.

For the system: potassium carbonate, ethyl alcohol, water, Cuno (Ann. Physik, *25*, 346) has shown that the different isotherms representing the binodal curve all cross at or near the plait-point, and this point would then be independent of the temperature and a solution at this point would not cloud (become inhomogeneous) on either warming or cooling. Solutions containing more alcohol than this critical solution will cloud on cooling but remain clear on heating, (*i. e.*, are at their upper critical temperature) while those with less alcohol cloud on warming but remain clear on cooling (are at their lower critical temperature).

A similar phenomenon in the system: dextrose, water, acetone, has been described by Krug and McElroy (J. Analyt. Appl. Chem., 1892, *6*, 153, 188); and Traube and Neuberg (Z. Phys.

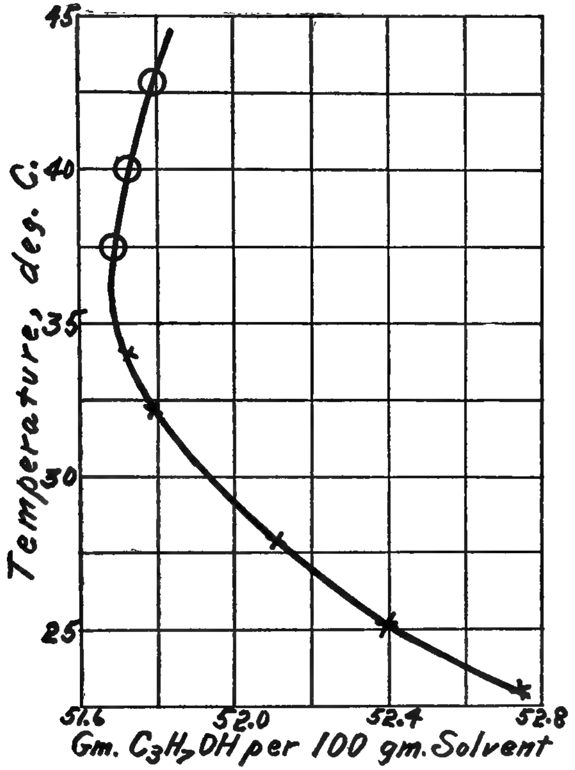


Figure 18

UPPER AND LOWER CRITICAL SOLUTION TEMPERATURES AT CONSTANT SALT CONTENT, IN THE SYSTEM: SODIUM CHLORIDE, NORMAL PROPYL ALCOHOL, WATER

Chem., 1887, *1*, 509) in the system: ammonium sulphate, ethyl alcohol, water, have found that the upper layer of two conjugate solutions is always at its upper critical solution temperature and the lower one at its lower critical temperature.

But Cuno also found that in the case of the lower ones of certain conjugate solutions, while they were at their lower critical temperature at 25°, an upper critical temperature could also be found above this. Thus with a solution containing 35.19% of carbonate by weight, the solution was inhomogeneous between 25 and 42°, while another solution containing 32.85% of the salt was inhomogeneous between 25 and 51°. A solution with 21.16% salt was clear below 25°, but cloudy from that point up to 80°, which was as high as it could be tested. Therefore, with increasing salt content in the upper layer, the temperature interval between the upper and lower critical temperatures increases, as does also the alcohol content of the solution. However, Snell (J. Phys. Chem., 1898, *2*, 457) showed that a solution containing 16.8% carbonate, 16.8% alcohol, and 66.4% water had a lower critical solution temperature of 40° and an upper one of 70°. This is very close to the plait-point as given by Cuno (30 gms. alcohol, 22.5 gms. carbonate, and 100 gms. water, or 14.75% carbonate) and would tend to throw doubt on the latter's statement. These determinations have been plotted in Figure 13, the two temperatures at which the solution just clears being joined. The plait-point is also indicated, and the apparent locus of the upper critical temperature for solutions having a lower critical temperature of 25°.

In Figure 14 will be found plotted the results we obtained for points on the isotherms at temperatures of 7.6 and 13.6°, and the general course of the isotherm for 25°. This was the upper one of a pair of conjugate solutions, and the isotherms therefore represent upper critical temperatures.

In the system: potassium fluoride, ethyl alcohol, water, no previous work has been done. Qualitative determinations which we have made indicate that the isotherms lie very close together, and the influence of temperature upon the binodal curve is small. Several homogeneous solutions were heated nearly to boiling and cooled in a freezing mixture without noticeable clouding, while one or two showed a trace of separation.

In the system: potassium carbonate, methyl alcohol, water, B. de Bruyn, (Z. Phys. Chem., *32*, 63) by determining the location of the quadruple point (vapor, two liquids, hydrate) at various temperatures, has concluded that as the temperature is lowered, the composition of the two liquid layers at the quadruple point becomes more nearly alike, until at about −35°, they become identical, hence below this temperature the liquid can exist in but one phase, *i. e.*, this is the lower limit of the lower critical solution temperature. He does not find that the isotherms in this system cross at all. It thus appears that the crossing of the isotherms at the plait-point is not a necessary condition in all systems.

The three systems involving propyl alcohol have never been studied before, and it was here that the influence of the temperature appeared to be the greatest. In the system containing potassium fluoride, at a content of about 21 gms. per 100 gms. solvent, cooling the solution from 25.6 to −3° increased the amount of propyl alcohol dissolved from 2.57 to 3.35 gms. per 100 gms. solvent. Points on the isotherms for several different temperatures were determined, and are plotted in Figure 15. In the same system, with a solution near the alcoholic end of the binodal curve (fluoride 0.533, water 29.93 and propyl alcohol 70.07 gms. per 100 gms. solvent) a lower critical solution temperature of 27° and an upper one of 41.5° could be clearly found.

In the system: potassium carbonate, propyl alcohol, water, an attempt was made to determine the effect of temperature changes on the solubility of the alcohol in solutions having a constant salt content. One of the solutions left from a determintion of the binodal curve was taken, its upper and lower critical solution temperatures determined, and an aqueous carbonate solution of the same strength made up. Small weighed portions of the latter were added, and the critical solution temperatures determined. The results are plotted on Figure 16. In an attempt to get another similar but more extended curve, more salt was added, the solution cooled to −12°, and water added in small portions with shaking. As the water warmed the solution, it was cooled after each addition, but it was noticed at one point, that the addition of the water partly cleared up the solution, but the cooling clouded it again. Suspecting the presence of another upper critical temperature, the solution was removed from the freezing mixture, and allowed to warm up. At −10° the solution cleared completely, but cooling for a fraction of a degree produced copious cloudiness. Careful examination failed to discover any separation of solid, so this appears to be a genuine upper critical temperature. On warming this solution to 60°, no separation was found. Upon now cooling to 25°, over 18 gms. of the alcohol had to be added to produce a separation into layers, showing that in this case the solution was unsaturated with respect to propyl alcohol at room temperature. As a matter of fact, comparison with the binodal curve showed the solution to contain 5% less alcohol than was required to saturate it at 25°. This solution, after adding the above-mentioned quantity of alcohol, was found to have a lower critical solution temperature of 23.5°, and an upper critical temperature of 57.6°. Upon now cooling below the lower critical solution temperature, a second upper critical solution temperature was found in exactly the same place as before, *viz.*, 10°. This is entirely out of harmony with the theory thus far developed, and it seemed best to leave this work to be continued later after procuring a supply of purer alcohol, so that the influence of any possible impurities might be eliminated. These results have also been plotted in Figure 16.

The influence of temperature upon the equilibrium in the case of propyl alcohol and sodium chloride is larger than in any other case here studied. A series of points on isotherms for various temperatures were determined and are plotted with the binodal curve in Figure 11. The course of the isotherms at these temperatures is indicated in Figure 17.

Some experiments were also performed with solutions containing more alcohol and less salt, both upper and lower critical solution temperatures being obtained. After making corrections for the variation of the salt content, the results plotted in Figure 18 were obtained. This represents graphically the influence of temperature on the solubility of the alcohol in solutions of a constant salt content (2.280 gms. per 100 gms. solvent). Here as in the system: potassium carbonate, propyl alcohol, water, some of the upper isotherms coincide with some of the lower ones.

SUMMARY

Six ternary systems of the class salt-alcohol-water have been investigated, and the complete curves for each worked out and drawn. In those which involve hydrated salts it is shown that the solubility of the salt is greater in absolute alcohol than when the alcohol is diluted with a small amount of water: in general, the solubility is about the same in absolute alcohol as in 60-70% alcohol.

A new method for the determination of ethyl alcohol has been worked out, and the results indicate that it is accurate in the presence of a small amount of methyl alcohol, if properly conducted.

It is shown for the first time that potassium fluoride has a very strong salting-out power for alcohols, and that its saturated solution is a better drying agent than a saturated solution of potassium carbonate, as it has a lower vapor pressure. The anhydrous salt itself is a good dehydrating agent, and more rapid than potassium carbonate on account of its greater solubility in organic liquids, at least in the alcohols here studied. It is also unique among drying agents of its class in the large per cent of water it will take up, to form the lowest hydrate.

A few experiments on the effect of temperature changes on the position of the binodal curve in the systems studied, show this influence to be very varying in quantity. Both upper and lower critical solution temperatures were obtained in the same solution in several cases, and apparently in one of the systems there exists a second upper critical temperature below the lower critical temperature.

ON THE POLYMERIZATION OF LIQUIDS AND A GENERAL METHOD FOR DETERMINING ITS RELATIVE VALUE

By M. M. Garver

Associate Professor of Physics in The Pennsylvania State College, State College, Pa.

In a recent paper[1] presented before the Royal Society of Canada at its May meeting, 1912, I applied a new molecular thermodynamic theorem to test, theoretically, the degree of polymerization of liquid substances. The dynamic basis of the theorem independently of its thermodynamic implications, may be concisely stated as follows:

The attractive forces which maintain a substance in the free liquid phase are just numerically equal to the pressure the same substance would exert, were it a perfect gas, at the same temperature and density.

The thermodynamic significance of this theorem lies in its furnishing the force function which may be applied in all isothermal changes of phase between liquid and vapor. From the fundamental equation for work, $W = \int_1^2 F\,ds$, we may always, theoretically, find the heat equivalent of the work when F can be expressed as a function of s, the displacement. When this function is expressed in terms of pressure and volume the above theorem leads directly to the conclusion that $\int_1^2 P dv = \mathrm{k} \int_1^2 \frac{dv}{v}$, which follows because it implies that the force, whether attractive, or exerting a pressure, is always proportional to the number of molecules acting on or through unit area. If we ignore the difference in sign, which alone distinguishes an attraction from a pressure, the force function is the same as that of the pressure exerted by a perfect gas. A number of experimental facts and theoretical reasons were advanced to establish the validity of the theoretical applications made. For details the former papers (*loc. cit.*) may be consulted.

---

[1] Jour. Phys. Chem. *16*, 455 (1912).

However, there is another aspect of the theorem to which attention never has been directed, so far as the writer is aware; but as it has special significance in connection with polymerization as the fundamental source of liquid stability it should be considered in connection with estimates of the degree of polymerization.

POLYMERIZATION AND LIQUID STABILITY

Probably the first impression made on most minds by the bare statement of the equality of the attractive and pressure relation of molecules contained in the above dynamical theorem is one of *instability*. If the forces are so delicately balanced whence comes the liquid stability with which we are all familiar? Why should the forces be just equal and not more or less? In a vague sort of way the molecules are generally regarded as held by some powerful attraction represented by thousands of atmospheres. It is perfectly evident on reflection that the whole attraction cannot exceed the sum of its parts or, that the attraction per unit area cannot exceed the sum of the pressures of the separate molecules acting in *one* direction through any element of area. The tension in a spring is measured by the pull on *one* end not by the sum of the pulls on the two ends. Likewise the force should be measured by the rate of change of momentum *normal to one side* of an element of area. This is what we call pressure and is what we should regard as the attraction also, since it is just sufficient to neutralize any pressure in the opposite direction. This view leads to the preceding theorem. The mathematically inclined may also doubtless reach the same conclusion through the application of D'Alembert's principle to a moving system of molecules.

THE SOURCE OF LIQUID STABILITY

Since the molecular forces in a free liquid must be in a state of equilibrium and the molecules are all relatively in motion with the same average speed of translation that they would have at that temperature were they perfectly gaseous, it is at once obvious that any *greater* force than that specified in the theorem would drive at least some of the molecules into contact, or union, and thus destroy their *relatively free motion*. It is also obvious that any *less* attractive force than that just sufficient to hold the molecules at the proper average distance would allow at least some molecules to escape and thus *cool* the remaining liquid. Let us call the union of two or more exactly similar molecules to form one, polymerization and the heat given out by the union, the heat of polymerization. (Since by Maxwell's law the average kinetic energy of translation is independent of the mass, such union must either increase the average *energy per molecule* of the system, or the system must give out heat.) With this in mind the part played by the polymerization in producing stability in the phase equilibrium is manifest. The union, or coalescence, of molecules must *raise* the average temperature of the remaining molecules and the escape of free vapor molecules must *lower* the average temperature by permitting additional molecules to de-polymerize. In consequence of this relation of polymerization to heat, the *stability of the system of balanced* forces which would otherwise be unstable, is maintained, so that the actual number of molecules can be disturbed, or changed, only by a transfer of energy in the form of heat or work, to or from the liquid. *The polymerization thus performs the function of a "source and sink" of heat energy and renders possible a stable equilibrium of freely moving independent molecules acted on by attractive forces,* without the intervention of any hypothetical repulsion.

RESOLUTION OF THE HEAT OF VAPORIZATION INTO COMPONENTS

During an isothermal change of phase from the vapor to the liquid phase, heat must be removed from the system of molecules in order to permit of the change. This heat, as we have seen, must consist of two parts, *first*—the heat of polymerization due to the decrease in the number of molecules, and *secondly*—the heat equivalent of the work due to all the forces acting during the process. It is easily seen that these two separate sources of the heat of vaporization, L, may be regarded separately and treated as independent of each other provided we are able to estimate the work due to the forces concerned. This we are able to do in the case of isothermal processes, by applying the theorem previously given, since the force at any instant depends upon the number of free molecules independent of polymerization. (The "force" is to be understood as independent of whether due to an external pressure or internal attraction.) Suppose we have N molecules occupying a volume V at a temperature T. Now suppose the volume to be decreased isothermally during which the heat L is given out and the combined external and internal forces do the amount of work W and the number of molecules is diminished by an amount n, the n molecules uniting with others, so that the number becomes N–n. From Maxwell's law and the principle of conservation, using the same units for heat and work:

$$W+\tfrac{1}{2}Nm_1u_1^2=L+\tfrac{1}{2}\,(N-n)\,m_2u_2^2$$

where L is the heat given out during the isothermal process. By Maxwell's law $\tfrac{1}{2}m_1u_1^2=\tfrac{1}{2}m_2u_2^2=\tfrac{1}{2}m\,u^2$, therefore

$$L-W=\tfrac{1}{2}n\,m\,u^2=H,\text{ or }L=W+H$$

where H is the heat of polymerization due to the decrease in the number of molecules occurring during the isothermal change from a vapor to a liquid.

A General Method of Finding the Relative Polymerization of two Liquids

At the time the previous paper was written it was not possible for me to do more than to show that all the liquids examined (many of which are regarded as non-associated,[1] or as consisting of simple vapor molecules) are according to the present theory, considerably polymerized. For the details of the theory and method of computation the former paper may be consulted. The quantities H and W and the ratio $r=\dfrac{L}{W}$ were found for thirteen different liquids of various different chemical types, but except in the case of water no estimate of the ratio of the weight of the liquid to the vapor molecule could be made, for no method of general application for such purpose had been found. Since then, however, further study of the subject has shown how the theory may be applied and used to determine the relative molecular weights of the liquid and vapor phases of any *other* liquid substance when these values are known for any *one* substance which may be used as a standard of comparison. In the case of water, as previously mentioned, it was possible, from certain available experimental data, to make a fair estimate of the relative molecular weights of the liquid and the vapor as lying between 2.5 and 1.9 at 0°C. The minimum value, 1.9 at 0°C., agrees with the value found by van der Waals[1] from entirely different considerations. In an early paper, W. Ramsay and J. Shields,[2] from surface tension experiments, found a value lying between 3 and 4; but in a later paper, Dr. Ramsay[3] reduced this estimate to 1.707 for water at 0°C.

---

[1] Nernst. *Theoretische Chemie.* 6te *Auf.* 282 (1909).

For the present paper the polymerization of water has been computed and tabulated at intervals of 20° from 0° to 200°C., and will be used later as a standard of comparison in computing the relative polymerization of the remaining dozen liquids discussed in the previous paper. The method will be found to be a perfectly general one and is not necessarily confined to the use of water as a standard. When any other substance becomes better known than water it may be used instead of water.

Let us consider any two substances S_1 and S_2 of which the molecular weights as vapor and also the values L and W previously explained, are known. Let m represent the molecular weight of the vapor and m' the molecular weight of the liquid, H_1 and H_2 the heats of polymerization, where $H=L-W$. The values L and H refer to one gram of the substance. Hm will then represent the heat of polymerization of a gram mol and must be proportional to the number of molecules that unite with others to form complex ones. Hence we have generally

$$\frac{H_1m_1}{H_2m_2}=\frac{n_1}{n_2} \qquad \text{(A)}$$

The quantity we wish to find is $\frac{m'}{m}$ which for brevity will be written x.

Since the total mass of n molecules is unchanged by polymerization we must have in the two cases

$$n\,m_1=n'_1m'_1 \text{ and } n\,m_2=n'_2m'_2$$

where n' represents the number of molecules of liquid. But

$$n-n_1=n'_1 \text{ and } n-n_2=n'_2$$

hence

---

[1] Zeit. phys. Chem. *13*, 715 (1894).
[2] Zeit. phys. Chem. *12*, 433 (1893).
[3] Zeit. phys. Chem. *15*, 115 (1894).

$$n=(n-n'_1)\frac{m'_1}{m_1}=(n-n_2)\frac{m'_2}{m_2}$$

By substitution and elimination we get finally

$$\frac{H_1m_1}{H_2m_2}=\frac{\frac{x_1-1}{x_1}}{\frac{x_2-1}{x_2}} \qquad \text{(B)}$$

where all the quantities are supposed to be known except x_2, that is, the ratio of the weight of the liquid to the vapor molecule of the substance investigated at the specified temperature, the value of x_2, however, depending upon the value x_1, of the liquid supposed known.

The method of finding the value of x for water was given in detail in the former paper (*loc. cit.*) and need not be repeated here. The above method to be strictly applicable must be used for the same temperatures. Hence the value of $x=\frac{m'}{\mathrm{m}}$ for water was first found for each 20° from 0° to 200°C. and tabulated in the accompanying Table I. The value of L at the different temperatures was found by applying Clausius' formula $L=607-.7t$ as being sufficiently accurate although it probably is not very reliable for high temperatures. The specific volumes for liquid and vapor water (saturated vapor) were taken from Winkelmann,[1] Matthiessen's values for the liquid being used from 0° to 100° and the table of Waterston for values from 100° to 200°. Battelli's values of the specific volumes of the vapor were used except for the temperature 160° which was omitted. The value 307.3 was taken from the table of Knoblauch, Linde and Klebe (p. 997). The remaining values are taken from the author's previous paper.

The value of L for most substances are most accurately known at their normal boiling points; hence it is desirable to have a standard liquid covering a wide range of temperatures. Hence the utility of the water table. From the degree of accuracy at present possible it was deemed sufficient to use 20° intervals in the construction of the table. The entire data are given in the table in order that the theory and results may be conveniently checked by those interested.

---

[1] Winkelmann, *Handbuch d. Physik* III, pp. 92–94, 996, 997.

TABLE I

POLYMERIZATION OF WATER, $\frac{m'}{m}$ (WITH DATA)

Temp.	Specific Volumes		Calories			$\frac{m'}{m}=x$
C.	Liquid	Vapor	L	W	H	
0		204000	607	365.6	241.4	2.11
20	1.0018	57730	593	351.7	241.3	2.02
40	1.0077	19484	579	338.2	240.8	1.93
60	1.0170	7650	565	325.5	239.5	1.86
80	1.0290	3401	551	313.3	237.7	1.80
100	1.0432	1667	537	301.5	235.5	1.75
120	1.0600	893.1	523	290.0	233.0	1.70
140	1.0795	511.4	509	278.6	230.4	1.63
160	1.1015	307.3	485	266.0	219.	1.58
180	1.1268	197.1	471	256.2	214.8	1.54
200	1.1578	130.6	457	244.8	212.2	1.51

Two illustrative examples of the method of computation will be given in some detail, and the results of the computation of the remaining twelve substances will be found in the column $\frac{m'}{m}$. The data for the computations are included in the table under appropriate column headings.

Attention was called in the previous paper to the necessity of taking into account possible polymerization of the vapor when determining the value of $H=L-W$ as the result gives only the *change* in the polymerization; but in the case of acetic acid I failed to profit by my own warning and used the theoretical molecular weight 60 instead of the actual which is about 97 according to its vapor density. The result was a value much too low and is corrected in the present table.

The following table gives data and values of $\frac{m'}{m}$ for all the substances for which I could obtain the necessary experimental data.

TABLE II

Substance	Temp. C.	Calories			Mol. Wt.	$\frac{m'}{m}$
		L	*W*	*H*		
Benzene	80	93.5	51.3	42.2	77.4	1.51
Carbon tetrachloride	20	51.1	28.6	22.5	153.7	1.61
Carbon tetrachloride	77	44.3	25.1	19.2	153.7	1.42
Carbon bisulphide	20	88.0	52.9	35.1	75.5	1.40
Ethyl ether	35	90.	44.3	45.7	73.6	1.59
Methyl formate	31.8	110	60.4	49.6	59.6	1.52
Methyl propionate	79.7	89	44.3	44.7	87.4	1.66
Ethyl acetate	77.	92.7	43.9	48.8	87.4	1.75
Propyl acetate	140	83.2	39.4	43.8	101.3	1.71
Methyl alcohol	66	262.0	134.0	128.0	31.8	1.78
Ethyl alcohol	78.4	216.4	91.5	124.9	46.	2.48
Propyl alcohol	97.4	166.3	71.8	94.5	60.	2.35
Acetic acid	118	97.	47.2	49.8	97.	1.905
Water	0	606.5	363.	240.5	18.	2.11
Water	100	537	300	237.	——	1.75

Let us take ethyl alcohol as the first example. Its boiling point 78° is near enough to 80° to allow us to use the data of water at 80°. Taking the necessary data from the tables we have for alcohol at 78°

$$\frac{H_1m_1}{H_2m_2}=\frac{\frac{x_1-1}{x_1}}{\frac{x_2-1}{x_2}}\qquad \frac{237.7\times18}{125\times46}=.744=\frac{.444}{\frac{x_2-1}{x_2}}\ \therefore\ x_2=2.48$$

For acetic acid at 118° we may use water at 120°

$$\frac{233\times 18}{49.8\times 97}=.868=\frac{.412}{\frac{x_2-1}{x_2}}\therefore x_2=1.9$$

In this case since the vapor was already 1.6×60 and underwent a further increase of 1.9 the total increase or actual liquid molecule is 1.6×1.9=3.1.

CONCLUSION

Particular attention is called to the functional part played by polymerization in maintaining equilibrium stability. The current impression that there exist immense internal pressures in liquids may conveniently be abandoned. They are dynamically impossible and otherwise serve no useful purpose. Unless we abandon entirely the Newtonian mechanics and the principle of D'Alembert the inwardly directed pressure cannot exceed the outwardly directed reaction, in a system of freely moving particles.

A very obvious objection that will no doubt be made at once by some physical chemists is, that the assumption of the perfect gas law as the law of force is unverifiable by experiment and is "too theoretical." The first reply to this objection should be that "the perfect gas law" actually assumed is entirely different from assuming that a given substance acts like a perfect gas or that it may be treated as a perfect gas because the internal attractions are negligible. The fundamental assumption that *is* made is one that is supported by the universally accepted principles of dynamics; and that is that the force of attraction which diminishes a pressure must be numerically equal, but opposite in sign, to the diminution in pressure produced by it. The *direction of the action* can have no influence on the *magnitude* of the work performed by it. So far as work is concerned it is immaterial whether it be done by a push or a pull or by a combined push and pull; and if the only effect of a pull is to diminish the push required and we know how much push would be required if there were no pull, then we may assume all push or all pull at pleasure without affecting *the computed amount* of the work due to the forces concerned. *The heat equivalent of work done by forces is* *entirely independent of the nature of the body upon which the work is done.*

A second reply might be: Suppose we admit that the fundamental assumptions are erroneous. Then the difficulty would be to explain the remarkable consistency of the results obtained and the practical agreement in many ways with the best results obtained by other methods. The values obtained for water are, of course, only a first approximation, but the *relative values* obtained, also depend upon the theoretically determined heat of polymerization. This is the fundamental basis of the whole theory; and the remarkable consistency of the results obtained would be even more wonderful considered as a system of accidentally balanced errors than as the "workings of a law of Nature."

THE RELATION BETWEEN THE POTENTIAL OF LIQUID AMALGAM CELLS AND THE CONSTITUTION OF THE AMALGAM

By Joel H. Hildebrand

University of Pennsylvania, Philadelphia, Pa.

In 1891 G. Meyer published his well-known research[1] on the molecular weights of certain metals as determined by the potential of amalgam cells, drawing the conclusion that the metals investigated dissolved in mercury as atoms. In 1902 Haber[2] called attention to the fact that Meyer's measurements do not decide between the case of a metal dissolved in mercury as single atoms and that of a hydrargyrate of the composition MHg_m. By calculating the osmotic work necessary to transfer the solute from one amalgam to the other on the assumption of a hydrargyrate being formed, he showed how the ordinary formula must be modified, and calculated the extent of the effect on the potential. However, as the amalgams become more concentrated an additional and uncertain cause of deviation arises in the inexactness of the gas-laws as applied to osmotic pressure except at great dilution. Hence it is unsafe to refer to the formation of hydrargyrates all deviations from the simple concentration formula,

$$nEF = RT \ \ln\frac{c_1}{c^1_2}.$$

Haber proceeds to show that an exact expression can be given only in terms of vapor pressure, and, by analogy with the equation applied by Dolezalek[3] to the lead accumulator, gives the equation,

$$nEF = RT\left(w_2 \ln p_2 - w_1 \ln p_1 - \int_{w_1}^{w_2} \ln p\, dw + m \ln\frac{p_2}{p_1}\right)$$

In this expression n denotes the valence of the dissolved metal, E, the e.m.f.; F the Faraday equivalent, R the gas-constant,

[1] Zeit. phys. Chem. *7*, 477 (1891).
[2] Ibid. *41*, 399 (1902).
[3] Zeit. f. Elektrochem. *4*, 349 (1898).

T the absolute temperature, w the number of mols of solvent mercury per mol of solute, p the pressure of mercury vapor over the amalgams, and m the number of atoms of mercury combined with one atom of the solute metal. The subscripts, 1 and 2 refer to the concentrated and dilute amalgams respectively.

Now, it would appear from this equation that if p were known as a function of w the expression could be integrated and the value of m determined which would satisfy measured values of E. The question of solvation would be thus settled beyond the shadow of a doubt. A closer examination of the equation, however, shows that the value of m cannot be so determined, and that a method so free from objection for the determination of solvation is not involved in the equation.

If N denotes the number of mols of mercury present, including both solvent and solvate mercury, then, since

$$N_1 = w_1 + m, \text{ and } N_2 = w_2 + m,$$

the equation becomes,

$$nEF = RT(N_2 \ln p_2 - N_1 \ln p_1 - \int_{N_1}^{N_2} \ln p dN).$$

This will be more evident if the expression is derived directly, by a process of isothermal distillation.

Let us imagine two large reservoirs containing concentrated and dilute amalgams, I and II, respectively. We can transfer one atom of the solute metal, M, from I to II electrically, as in a concentration cell, whereby the work nEF would be gained. The same transfer may be made by isothermal distillation as follows.

1. Remove from I 1 mol MHg_m together with the corresponding solvent mercury, $N_1 - m$ mols. This requires no work.

2. Distill into this portion from II enough mercury vapor to bring it to the same concentration as the amalgam in II. The amount distilled is $(N_2 - m) - (N_1 - m)$, or, $N_2 - N_1$, and the work done is

$$RT \int_{N_1}^{N_2} \ln \frac{p_2}{p} dN.$$

3. The separated portion is now of the same concentration as the amalgam in II and is added to it without doing any work.

4. We have now transfered from I to II $N_1 - m$ mols of solvent mercury and m of combined mercury, or N_1 mols altogether, in addition to 1 mol of the metal M. To make the process equivalent to the electrical transfer, we have finally to distill back into reservoir I N_1 mols of mercury, doing the work,

$$N_1 RT \ln \frac{p_2}{p_1}$$

Equating the total work done in the distillation process to the electrical work, we have,

$$nEF = RT\left(N_1 \ln \frac{p_2}{p_1} + \int_{N_1}^{N_2} \ln \frac{p_2}{p} dN\right) = RT\left(N_2 \ln p_2 - N_1 \ln p_1 - \int_{N_1}^{N_2} \ln p dN\right).$$

It will be noticed that wherever m occurs it cancels out, and so does not appear in the final equation.

Now, this expression can be still further simplified by putting

$$\int \ln p dN = N \ln p - \int N d \ln p.$$

whence we obtain as the final form,

$$nEF = RT \int_{N_1}^{N_2} N d \ln p; \text{ or } nEF = RT \int_{N_1}^{N_2} \frac{N dp}{p}.$$

It must not be inferred from this that the potential of amalgam cells should be unaffected by the formation of hydrargyrates, for though m does not appear in the equation as given it is involved in any expression giving p as a function of N which we may use to integrate the final equation for e.m.f. here given by the writer.

We will now show how this equation can be integrated using the vapor pressure law to take into account the constitution of the amalgams involved.

Very accurate measurements of the potentials of amalgam cells have been made in recent years in the Harvard[1] and Princeton[2] laboratories. These measurements have shown that the gas-laws hold accurately at high dilutions, but that considerable deviations occur at greater concentrations, the direction depending upon the solute metal. Thallium, indium and cadmium give potentials greater, and zinc, lead and tin smaller than those calculated from the simple concentration formula. A number of methods of accounting numerically for these differences are used by Richards and his co-workers, but while the energy changes are rather well accounted for thermodynamically, the effect of polymerization or solvation is merely considered qualitatively, and that chiefly in the case of zinc, showing in a general way that the deviations are in the direction expected.

---

[1] Richards and Forbes, Pub. Carnegie Inst. No. 56, and Zeit. phys. Chem. *58*, 683 (1907). Richards, Wilson, and Garrod-Thomas, Pub. Carnegie Inst. No. 118, and Zeit. phys. Chem. 72, 129, 165 (1909).

[2] Hulett and DeLury, J. Am. Chem. Soc. 30, 1812 (1908). Crenshaw, J. phys. Chem. *14*, 158 (1910).

Let us suppose that the dissolved metal forms a solvate with the mercury of the general formula MHg_m. Then, if the solution is made from 1 mol of M and N mols of mercury, the solvent mercury would be $N-m$ mols, and the total number of mols would be $N-m+1$. Using these values for the mol-fraction of mercury in the vapor pressure law,[1] which states that the pressure of a component over of a mixture is proportional to its mol-fraction in the mixture, the proportionality constant being the saturation pressure of the pure component p_o, we get the equation,

$$p=p_o\frac{N-m}{N-m+1}.$$

If this function of p in terms of N is used to integrate the general formula deduced above, the resulting equation is

$$E=\frac{2.3026RT}{nF}\left[m\log\frac{N_2-m}{N_1-m}-(m-1)\log\frac{N_2-m+1}{N_1-m+1}\right].$$

In applying this formula we will consider the case of thallium amalgams. Freezing point data have furnished definite evidence of the existence of the compound $TlHg_2$ in the solid state. In Table I are given the results of Richards and Wilson[2] on the potential of thallium amalgams at 30° compared with the results calculated from the ordinary concentration equation and from the equation just given, using for m the values X, 2, 5, and 6 successively. It will be seen that the value $m=2$ improves the agreement with the measured potentials considerably, a much better agreement is gotten from the value 5 or 6.

We must conclude from this that dilute thallium amalgams contain the compound $TlHg_6$. It will be interesting to confirm this by means of measurements of vapor pressure of thallium amalgams.

[1] Cf. preceding paper.

[2] l.c.

TABLE I

%Tl	N	Potential in millivolts at 30°				
		Observed	Calculated from			
			c/c^1	$TlHg_2$	$TlHg_5$	$TlHg_6$
1.8456	54.2					
		37.13	32.78	34.42	36.60	37.42
0.5249	193.5					
		22.61	21.61	21.90	22.32	22.52
0.2294	443.5					

Let us now apply to the fundamental equation for e.m.f. the vapor pressure measurements made by the writer[1] on zinc amalgams. It has been shown that the vapor pressures of zinc amalgams are given quite accurately by the equation,

$$\frac{p}{p_0} = \frac{2N(K+4)}{N(K+8)+K+4+\sqrt{(KN+K)^2+4K(2N+1)}},$$

where K is the equilibrium constant of the reaction,

$$2Zn = Zn_2,$$

as given by the equation,

$$\left(\frac{1-2\alpha}{N+1-\alpha}\right)^2 = K\frac{\alpha}{N+1-\alpha},$$

in which α represents the number of mols of Zn_2 produced. α is gotten in terms of K and substituted in the vapor pressure law which, in this case, is expressed as

$$\frac{p}{p_0} = \frac{N}{N+1-\alpha},$$

In order to integrate the expression

$$nEF = RT\int_{N_1}^{N_2} Ndlup$$

we can write, since α is small when N is large, a condition fulfilled in the e.m.f. measurements we shall use,

$$\frac{I}{N} = K\alpha.$$

---

[1] Cf. preceding paper.

If the value K=0.50 holds at lower temperatures than

$$\frac{p}{p_0}=\frac{N}{N+1-\frac{2}{N}},$$

and

$$\frac{p}{p_0}=\frac{N^2}{N^2+N-2}.$$

Using this equation in the above integration, we get for the e.m.f. of zinc amalgams

$$E=\frac{2.3026\,RT}{2F}\left(2\log\frac{N_2+2}{N_1+2}-\log\frac{N_2-1}{N_1-1}\right)$$

To test this equation we have both the measurements of Richards and his co-workers[1] and those of Crenshaw.[1] Table II gives observations of Richards and Garrod-Thomas on the potential of the most concentrated amalgams used. Compared with the observed values are given those calculated from the ratio c_1/c_2 and from the equation just derived by the writer.

In Table III are given similar figures for the amalgams measured by Crenshaw, which extend to much higher concentrations, where the deviations from the gas-law equation are very great. Here again, however, the potentials calculated from p are in excellent agreement with the observed potentials, the slight deviations being in the direction produced by the simplifying assumptions made in integration.

It may seem strange that the value of K obtained at 300° should apparently remain the same at ordinary temperatures. It is by no means impossible, even though somewhat unusual. The constancy of K is borne out in a rather imperfect way by the vapor pressure measurements. The ration p/p_0 seemed to be independent of temperature, although careful measurements of this ratio at a widely differing temperature have not yet been made.

It must be emphasized, finally, that even though it were shown that the experimental values of the relation between p and N are not due to association of zinc atoms, nevertheless, the course of the vapor pressure curve, and therefore the potentials calculated from it, remain the same, and therefore in agreement.

---

[1] l.c.

It may be concluded, therefore, that the equation here given by the writer is confirmed by the behavior of zinc, and the probable behavior of thallium amalgams. The writer hopes soon to be able to report measurements upon thallium and other amalgams.

TABLE II

%Zn	N	Potential in milli-volts. 30°		
		Observed	Calculated from	
			p	c_1/c_2
0.900	36.0			
		10.18	10.18	11.13
0.384	84.9			
		6.12	6.18	6.45
0.234	139.4			

TABLE III

$\frac{\text{grams Zn}}{\text{grams Hg}}$	N	Potential in milli-volts. 25°		
		Observed	Calculated from	
			p	c_1/c_2
2.20/100	14.86			
		0.89	0.87	1.34
2.00/100	16.36			
		0.94	0.98	1.35
1.8/100	18.17			
		2.43	2.48	3.23
1.4/100	23.35			
		3.54	3.57	4.32
1/100	32.70			
		7.83	7.93	8.90
5/1000	65.37			

THE VAPOR PRESSURE OF ZINC AMALGAMS

BY JOEL H. HILDEBRAND
University of Pennsylvania, Phila., Pa.

Among the greatest triumphs of modern science must be reckoned the discovery and application of the laws governing dilute solutions, which may be grouped under the general idea of the application to solutions of the Rule of Avogadro. In all the development of chemistry there have probably been no principles which have proved to be such valuable instruments in the hands of investigators. However, the increasing deviations from these laws shown as solutions approach ordinary concentrations have produced the conviction that Avogadro's Rule as applied to solutions must be regarded as an extrapolation, and that a more exact law, applicable to concentrated solutions, must be established. The Law of Raoult for the lowering of vapor pressure, announced from a purely empirical basis, has more recently received the theoretical foundation and experimental proof which indicate that it is probably the nearest approach that we possess to an exact law of a perfect solution.

The problem has been clearly stated and its solution indicated by Nernst where he states,[1] "wir dürfen die aktive Masse des Lösungsmittels proportional der Koncentration des von ihm entsandten Dampfes setzen. . . . Dies Resultat wäre durch kinetische Betrachtungen nicht zu erhalten gewesen und ist auch erst von mir auf diesem Wege gefunden worden. Die Thermodynamik vermag uns also herin weiter zu führen, und es sei betont, dass bei der Behandlung konzentrierter Reaktionsgemische sie allein gegenwärtig die theoretische Führung zu übernehmen im stande ist, wären wir im Besitze von Regeln über die Dampfdrucke beliebig konzentrierter Gemische, so würden wir die Reaktionen solcher Systeme mit der gleichen Vollständigkeit behandeln können wie diejenigen verdünnter Lösungen." The vapor pressure of one component of a mixture is thus the direct measure of the "active mass" of the component in the mixture. The experi-

---

[1] Theoretische Chemie, 5th ed., p. 647.

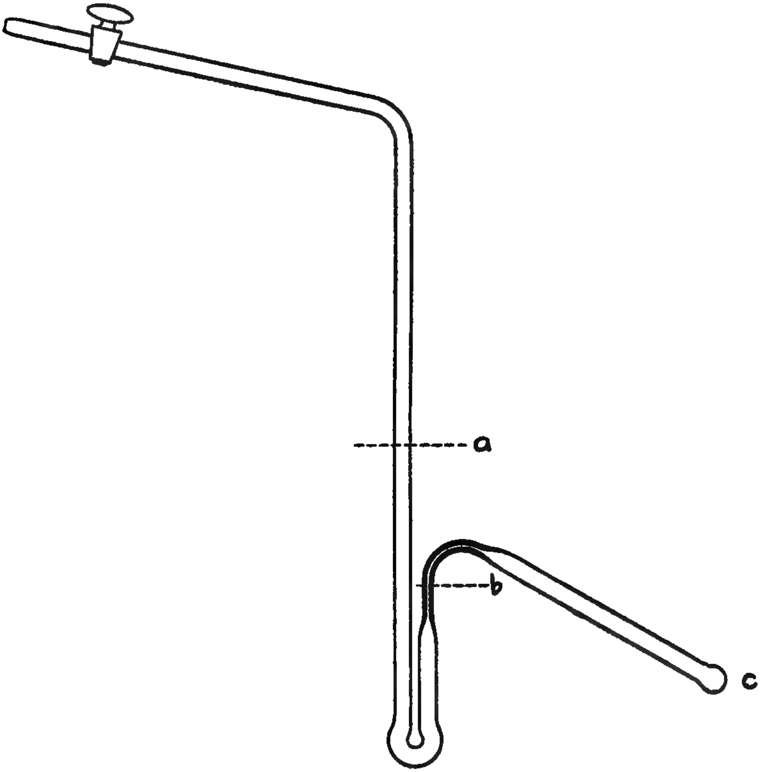


Figure 1

mental advantage of referring active mass to vapor pressure rather than to osmotic pressure, for example, is obvious.

Now, the other side of the equation involves the expression of active mass in terms of the quantities of material present. This seems possible by following the suggestion originally made by Gibbs, and advocated since by Plank, van Laar and others, that the active mass of a component of a phase is proportional to its mol-fraction, *i.e.*, to the number of mols of the component divided by the total number of mols present. Combining this with the above expression of Nernst, we have the law that *the vapor pressure of a component of a mixture is proportional to its mol-fraction.*

The constant of proportionality is given by making the mol-fraction 1, which shows it to be the vapor pressure of the substance in the pure state, that is, of the saturated vapor. The value of this law has been emphasized by a number of authors recently, among whom may be mentioned Dolezalek,[1] Lewis,[2] Möller,[3] and Washburn.[4] The interesting results of Dolezalek in determining the constitution of liquid mixtures and the importance of a reliable method of investigating the various problems of association, dissociation, and solvation, make, as Washburn says, the gathering of data along this line of great importance.

This study of the vapor pressure of amalgams was begun with the double purpose of testing the vapor pressure law upon solutions differing widely in physical nature from the organic mixtures to which it has hitherto been applied, and also of attacking the general problem of metal compounds from a new standpoint.

While the compounds of the metals with one another have been largely investigated in recent years by thermal analysis, the results so obtained allow nothing but inference concerning the nature of the liquid phase. The well-defined and varying physical constants of the metals promise much of interest as a result of a thorough study of their solutions in one another. The natural starting point of such a series of investigations is the amalgams, since they are liquid at not too extreme temperatures, and have measurable vapor pressures, allowing, therefore, their investigation by means of the vapor pressure law. The published work in this direction is very limited. The existence of hydrargyrates in solution has been the subject mainly of speculation.[5] The vapor pressures of very dilute amalgams have been studied in the comprehensive work published by Ramsay[6] a number of years ago, but the molecular weight of the metals was the object in view, and no conclusions were drawn regarding possible solvation although such is clearly indicated in several cases.

In the light of what has been said it is evident that a further study of this problem using more concentrated solutions is of

[1] Zeit. phys. Chem. *64*, 727 (1908); *71*, 191 (1910).

[2] Journ. Amer. Chem. Soc., *30*, 668 (1908).

[3] Zeit. phys. Chem. *65*, 226 (1909).

[4] Journ. Amer. Chem. Soc., *32*, 653 (1910).

[5] See Berthelot, Ann. Chim. phys. 5 *18*, 433. Haber, Zeit. anorg. Chem. *44*, 399 (1902); G. MacP. Smith, Zeit. anorg. Chem. *58*, 381 (1908).

[6] Journ. Chem. Soc. *55*, 521 (1889).

considerable importance. The results upon zinc amalgams here presented are the first of a series which the writer hopes to carry out.

EXPERIMENTAL PART

1. *Materials Used*

The mercury used was first washed in the apparatus described by the writer,[1] and then distilled as prescribed by Hulett.[2] The zinc was "Baker's Analyzed," the analysis giving 0.05% of lead, 0.004% of iron, no arsenic, and a trace of cadmium. An analysis made to confirm these figures gave 0.04% lead and 0.001% of iron. These amounts were far too small to influence the results.

2. *Apparatus*

For the purpose of measuring the vapor pressure the amalgams were confined in tubes such as shown in Fig. 1. The internal of this tubing was about 7 mm., thus minimizing the effect of the surface tension of the amalgam. In the first experiments the part between *b* and *c* was lacking. The part from *a* around to *b* was blown separately and fused onto the upper part after putting into it a weighed piece of zinc, which had previously been moulded into thin sticks and scraped free from surface oxide. The tube containing the zinc was then exhausted and enough mercury admitted carefully from a supply poured in beyond the stopcock to furnish an amalgam sufficient to fill the closed limb of the U-tube and extend well around the bend. The quantity of mercury used was determined after the experiment by cutting at *a*, and weighing the U-tube with and without amalgam. The amount of zinc being known, the mercury was given by difference. Vacuum reductions were not made, as the corrections thus made would have been beyond the limits of accuracy otherwise attainable. The tube now containing the mercury and zinc was heated while still exhausted, whereby the zinc amalgamated with the mercury and at the same time the short limb was boiled free from residual gas. The tubes were drawn to a point at *b* so that a minute bubble of gas could be easily seen. In the later experiments with more concentrated amalgams, Nos. 29 to 32, it was found necessary, in order to avoid the presence of oxide, to fill the tubes

---

[1] J. Amer. Chem. Soc. *31*, 933 (1909).

[2] Phys. Rev. *33*, 307 (1911).

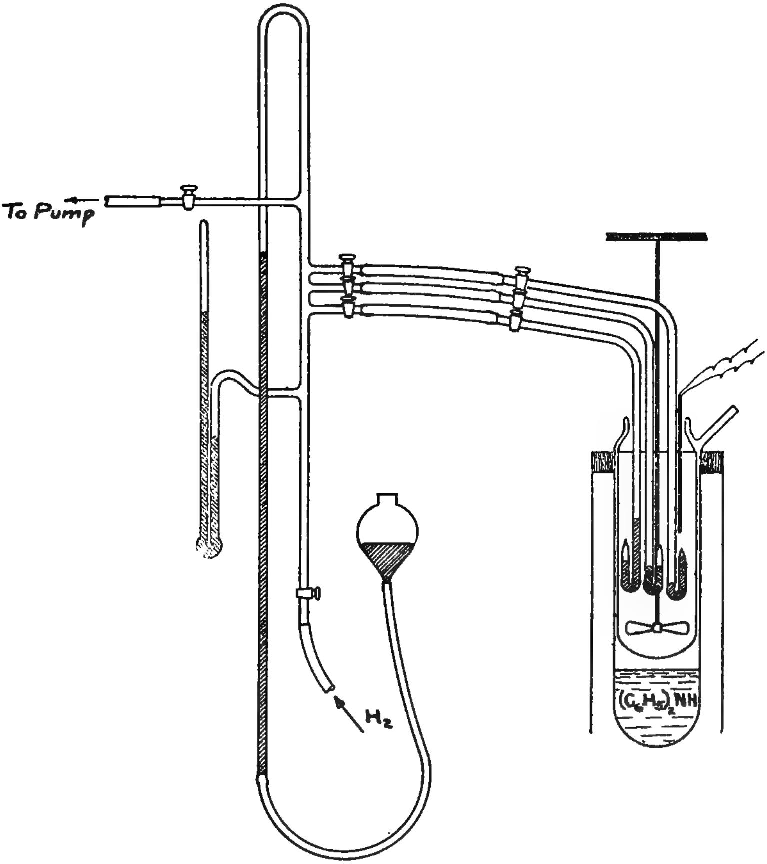


Figure 2

in a different manner. The tube was blown as shown in the figure except that it was left open at *c*. After introducing the weighed zinc at *c*, it was sealed at this point, the mercury introduced in a weighed amount at the other end, whereupon the tube was exhausted, filled with hydrogen and again exhausted. The mercury was then run into *b-c*, and hydrogen admitted to a pressure of slightly less than one atmosphere. On heating, the zinc amalgamated with the mercury and the amalgam was run through the capillary into the U leaving behind the small amounts of oxide which had collected on the surface. The capillary was sealed at *b*, leaving the tube ready for insertion into the thermostat. A similar tube containing mercury alone, and filled, of course, without the above precautions, served to give the vapor pressure of mercury for comparison.

The measurements were carried out at 300° in a thermostat shown in Fig. 2, and constructed for the writer by the Caloris Company of Philadelphia. It was constructed on the plan of a vacuum bottle, the outer bottle was elongated so as to contain the heating liquid, diphenylamine, whose vapors heated the liquid in the inner bottle. This latter was ordinary commercial "Cottolene." The side tube shown in the figure served as an air-condenser for the vapors of diphenylamine not condensed in the lower parts of the apparatus. The cottolene, protected from the air as much as possible by asbestos coverings, stood the high temperature fairly well. It gave off endurable quantities of acrolein and had to be replaced after two days' use on account of darkening. The apparatus was protected on the outside by a cylinder of glass cut from a tall beaker, and the space between the top of this cylinder and the bottle was closed by a roll of asbestos paper. The cottolene was stirred vigorously by a stirrer, as shown, run at a high speed by an electric motor. The temperature was determined by means of a copper-constantin thermocouple, the cold junction of which was kept in ice in a vacuum bottle. The e.m.f. of the couple was read on a Siemens-Halske galvanometer. The temperatures given later are, however, taken from the vapor pressure of the mercury as given by the careful measurements of Smith and Menzies.[1]

The vapor pressure of the mercury and amalgams at this temperature tends to make the liquid fall in the closed limb of the U-tubes, and this was balanced and measured with the aid of the connections shown in the left of Fig. 2. The tube containing the mercury and two containing amalgam were connected as illustrated, and the apparatus, including the rubber connections, pumped free from air. The cocks of the U-tubes were then opened and hydrogen, from a Kipp-generator, purified by passing over a heated copper spiral and drying with sulphuric acid, was admitted to a pressure sufficient, as the temperature of the thermostat rose to 300°, to keep the level of the amalgam in both limbs of one of the tubes approximately the same. Finer adjustment of pressure was made by means of the reservoir of mercury shown in the figure. This method of adjusting pressure seems easier than that used by Smith and Menzies.

---

[1] J. Amer. Chem. Soc. *32*, 1434 (1910).

The pressure adjusted so that the mercury stood at the same level in one of the tubes, the greater pressure in the closed limb of the tube containing the pure mercury forced the mercury to rise in the other limb to an amount equal to the difference in pressure of the amalgam and of mercury. This difference in level was read by means of a cathetometer, simultaneous readings being taken on the manometer giving the pressure of the amalgam direct. A number of readings were taken with each tube, the pressure being readjusted before each reading. The pressure was also frequently increased to make sure of the absence of gas in the closed limbs. All readings were reduced to mm. of mercury at 0°. The readings on the cathetometer, being in mm. at 300°, were reduced by the factor 0.947, which is the ratio of the density of mercury at 300°, 12.881, to that at 0°, 13.596.

In experiments 29-32, the difference in pressure had become too great for the dimensions of the thermostat, also the mercury showed a tendency to boil in the open limb, so that a second apparatus similar to that shown on the left of the figure was used in connection with the U-tube of mercury. The mercury in this tube was now also adjusted to the same level and the pressure read independently on the attached manometer. The extra connections and the use of hydrogen were dispensed with in this part of the apparatus. This arrangement proved more satisfactory than the former where a cathetometer had to be used, and will doubtless be retained in future investigations.

3. *Results*

Table I gives a typical experiment, No. 31. In this, P_0 denotes the vapor pressure of mercury; P, that of the amalgam; N, the number of mols of mercury per mol of zinc. It will be seen that the slight changes in temperature affect the pressures in the same ratio, so that the simultaneous determination of the pressures made it useless to seek greater constancy in temperature.

Table II gives a summary of all the data secured, each line representing results similar to those of Table I. The values of the relative pressures, P/Po, are plotted in the curve, Fig. 3, against the atom-per cent of zinc, N/N+1, given in the fifth column of the table. If the amalgams were perfect solutions and obeyed the law $P/P_o = N/N+1$, then the graph should be a straight line, and the values in the sixth and seventh columns of the table should agree. It will be seen that the pressures are considerably higher than they should be for a simple solution.

TABLE I

Expr. No. 31. Wt.Zn = 6.712; Wt.Hg = 12.230

P	P_o	P/P_o	Temp.
111.9	241.8	0.463	299.4
108.9	240.8	0.453	299.0
112.4	241.3	0.466	299.1
111.9	241.3	0.464	299.1
108.9	237.8	0.458	298.5
109.9	238.8	0.460	298.7
110.9	240.8	0.461	299.0
111.9	241.3	0.463	299.1
112.9	242.1	0.466	299.5
		Mean 0.462	

TABLE II

No. of Expr.	No. of Observ.	%Zn	N	$\frac{1}{N+1}$	$\frac{1}{N+1}$	$\frac{P}{P_o}$	$\frac{N}{N+1-\alpha}$	Δ
21	6	2.655	11.98	0.077	0.923	0.928	0.930	−0.002
8	9	3.72	8.461	0.107	0.893	0.906	0.906	+0.000
22	5	4.61	6.776	0.129	0.871	0.884	0.887	−0.003
6	10	5.74	5.353	0.158	0.842	0.854	0.863	−0.009
19	7	10.00	2.946	0.254	0.746	0.787	0.786	+0.001
12	6	10.63	2.747	0.267	0.733	0.771	0.774	−0.003
17	6	10.66	2.745	0.268	0.732	0.778	0.773	+0.005
20	5	11.75	2.458	0.290	0.710	0.743	0.756	−0.013
24	5	12.76	2.238	0.309	0.691	0.735	0.739	−0.004
18	4	13.74	2.056	0.328	0.672	0.718	0.725	−0.007
32	7	17.78	1.510	0.398	0.601	0.675	0.665	+0.010
25	8	19.52	1.348	0.426	0.574	0.658	0.642	+0.016
28	3	19.70	1.332	.429	0.571	0.644	0.638	+0.006
26	6	19.80	1.325	0.431	0.569	0.649	0.636	+0.013
30	5	26.00	0.929	0.519	0.481	0.561	0.559	+0.002
29	8	30.42	0.747	0.572	0.428	0.501	0.501	−0.006
31	9	35.45	0.595	0.627	0.373	0.462	0.454	+0.008

How can these deviations be accounted for? This was done by assuming, as Dolezalek has done, that the solute is associated to some extent, and hence the number of mols of zinc is less than is assumed in the simple formula.

Suppose that the atomic mols of zinc unite partially according to the equation,

$$2Zn = Zn_2.$$

If a represents the number of mols of Zn^2 formed from 1 mol of Zn, there would remain $1-2a$ mols of Zn, and the total number of mols present in the mixture would be $N+1-a$. Applying the law of mass-action, using mol-fractions instead of concentrations, we obtain the equation:

$$\left(\frac{1-2a}{N+1-a}\right)^2 = K\frac{a}{N+1-a}$$

Solving this equation for a, we get

$$a = 0.5 + \frac{KN - \sqrt{(KN+K)^2 + 4K(2N+1)}}{2(K+4)}$$

(The minus sign before the radical is evidently correct.) Now, since the relative pressure should be equal to the mol-fraction of mercury:

$$\frac{P}{P_0} = \frac{N}{N+1-a}$$

Substituting the above value of a in this equation we obtain:

$$\frac{P}{P_0} = \frac{2N(K+4)}{N(K+8)+K+4+\sqrt{(KN+K)^2+4K(2N+1)}}$$

The values given in the eighth column of Table III and represented by the curve in Fig. 3 were obtained by putting

$$K = 0.50,$$

when the equation becomes:

$$\frac{P}{P_0} = \frac{9N}{8.5N+4.5+\sqrt{0.25N^2+4.5N+2.25}}$$

The last column, Δ, in the table gives the differences between the observed values of P/P_0 and $N/N+1-a$, calculated by this equation. The closeness with which the results agree is very striking, admits of hardly any other conclusion than that the assumptions involved are correct. If zinc is associated in solution in mercury, then the vapor pressure law expresses the behavior of the solution up practically to the limit of the solubility of zinc in mercury at this temperature.[1]

---

[1] 70.5 atom per cent zinc, according to Puschin, Zeit. anorg. Chem. *36*, 201 (1903).

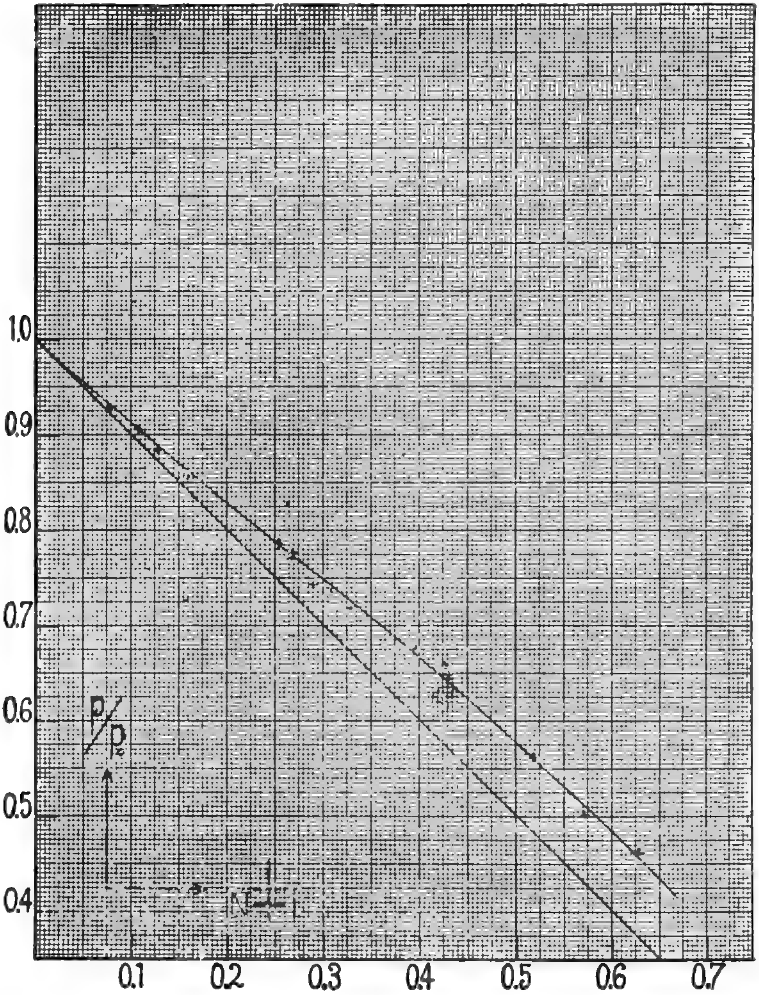


Figure 3

It is interesting, furthermore, to note the extent of the association at various concentrations, calculated from the value of K = 0.5,

N	100	10	1	0
Per cent association	4	22	52	66.7

If zinc could exist in the liquid state at 300° it would accordingly be $\frac{2}{3}$ associated to Zn^2.

CONTRIBUTIONS TO THE CHEMICAL KINETICS OF ENZYMES

By Kikunaë Ikeda
Imperial University of Tokyo, Japan

The gradual decay of the enzymes in the course of the reactions is one of the factors which make exact study of enzymatic actions so very difficult. For the further progress of this important branch of chemical kinetics, it is, therefore, necessary that this problem should be thoroughly investigated. In the following the results obtained on some special points of the subject are communicated.

As there is hardly any doubt that enzymes are of colloidal nature, the theoretical treatment would be hopelessly complicated if the cases were studied in which the substrata are also colloids. Hence the present investigation is limited to the cases where the substrata form genuine solutions.

As enzymes are known at present only as activities and not as substances, the unit in which the concentration or the quantity of an enzyme is expressed should be such as corresponds to unit catalytic action. Assuming the reaction not to be markedly reversible, the velocity may be represented by the equation:

$$\frac{dC}{dt} = -HC_1^{n_1}C_2^{n_2}\ldots\ldots, \qquad (1)$$

where C_1, C_2, etc., represents the concentrations of the reacting substances, n_1, n_2, etc., molecular coefficients, t time and H the catalytic activity of the enzyme. Here it is assumed that the reaction is infinitely slow in the absence of the enzyme. In the great majority of well-studied cases H has been found to be proportional to the concentration of the enzyme.
Or

$$H = kE, \qquad (2)$$

where k is the velocity coefficient and E the concentration of the enzyme. K is a function of experimental conditions, more particularly of temperature and coexisting substances. If T represents temperature, and S_1, S_2, etc., the concentrations of the co-existing substances, then

$$k=\phi(T,\ S_1,\ S_2,\ \ldots\ldots). \qquad (3)$$

The velocity with which the enzyme is destroyed is determined by temperature, the reacting and co-existing substances. Hence—if E_o is the initial concentration of the enzyme,

$$E=\psi(E_o,\ T,\ C_1,\ C_2\ldots\ldots,\ S_1,\ S_2,\ldots\ldots). \qquad (4)$$

The specific feature of the chemical kinetics of enzymes consists in the study of functions (3) and (4). The influence of the co-existing substances is most varied and full of interest. The effect of various excitants and retarding agents falls under this head, and the difference in the behaviour of the same enzyme from different sources will doubtless be traced to such influences. But our present knowledge is too meagre to venture any generalization on this point. We shall therefore treat here only such cases, in which the effect of S_1, S_2, etc., is negligibly small or remains unchanged throughout. Then equations (3) and (4) reduce to

$$k=\phi\ (T) \qquad (5)$$

$$E=\psi(E_o,\ T,\ C_1,\ C_2,\ \ldots\ldots,\ t) \qquad (6)$$

Equation (5) must have the same form as in ordinary chemical kinetics. As the temperature range, over which an enzymatic action can be studied, is necessarily very limited, the effect of temperature upon k can be equally well represented by either of the following equations:

$$k=e^{a(\delta-\delta')}, \qquad (7)$$

or

$$k=e^{\alpha\left(\frac{1}{\tau}-\frac{1}{T}\right)}, \qquad (8)$$

where δ is the temperature in degrees centigrade, δ' the standard temperature at which $k=1$; τ is the same temperature in the absolute scale, and a and α are constants. At the standard temperature equation (2) reduces to

$$H=E.$$

It is usually supposed, in analogy to inorganic catalysers, that a definite quantity of an enzyme can transform an infinite amount of the substratum. This can only be the case where temperature is kept so low, that the velocity of decay of the enzyme through the effect of heat is immeasurably small. But even then it is doubtful whether this can be strictly true. At any rate, the weakening of the enzyme in the course of the reaction is a fact of tolerably general observation. The rate of decay of the enzyme may stand in a very complicated relation to that of the main reaction, but the most probable assumption is that they are proportional to each other. In other words, the destruction of the enzyme takes place in accordance to its catalytic activity, or mathematically expressed:

$$\frac{dE}{dt} = r\frac{dC}{dt}. \qquad (9)$$

In order to form a clear mental image of the mechanism of the catalytic activity of the enzyme as well as that of its decay, let us take the particular case of the decomposition of hydrogen peroxide through the agency of catalase. The velocity of the reaction must be proportional to the number of molecules of hydrogen peroxide, which are in contact with the particles of the enzyme. At every moment this must be proportional to the product of the concentrations of the enzyme and the peroxide. Hence,

$$\frac{dC}{dt} = -kEC. \qquad (10)$$

This is the equation which Senter has demonstrated to hold in the case of blood catalase, when the temperature is low and the concentration of hydrogen peroxide is very small. Indeed, the velocity of a large number of enzymatic reactions is represented by equation (10).

If the enzyme is destroyed by an interaction with hydrogen peroxide, the velocity of destruction must also be proportional to the number of molecules of the peroxide which are in contact with the particles of the enzyme. Hence we may write:

$$\frac{dE}{dt} = -k'EC, \qquad (11)$$

where k′ is the velocity coefficient of the decay of the enzyme. Whatever the nature of the interaction between the enzyme and the substratum may be, it is quite indifferent to the establishment of equation (11). But it is quite probable that catalase is destroyed by oxidation, because other oxidizing agents have also very injurious effect upon it.

From (10) and (11) we have

$$\frac{dE}{dt}=\frac{k'}{k}\ \frac{dC}{dt}, \qquad (12)$$

which is in agreement with (9). From the foregoing it is clear that this equation must hold also in great many cases, where the enzyme is acted upon by the substratum.

Integrating equation (12) we get the relation:

$$E=\frac{k'}{k}\Bigl(A+C\Bigr), \qquad (13)$$

where

$$A=\frac{k}{k'}E_0-C_0, \qquad (14)$$

C_0 being the initial concentration of the substratum. It is important to remember that the value of A becomes positive, negative or zero according as kE_0 is greater or less than $k'C_0$ or is equal to it. Equation (13) is a particular case of equation (4) or (6).

Putting this value of E in (10), we have

$$\frac{dC}{dt}=-k'(A+C)C, \qquad (15)$$

from which we see that the reaction may be formally considered to be one of the second order, in which the initial concentrations of the reacting substances differ by the amount A, and the velocity coefficient of which is k'. Equation (15) gives on integration:

$$\ln\frac{C_0}{C}-\ln\frac{C_0+A}{C+A}=k'At, \qquad (16)$$

or

$$C=\frac{k'AC_0}{kE_0 l^{k'At}-k'C_0} \qquad (17)$$

If A is positive, the denominator of the right side of equation (17) grows continuously larger with increasing t, so that C must gradually approach zero. In other words, the reaction proceeds to completion with time. This will be the case if the initial concentration of the enzyme is relatively large in comparison to that of the substratum.

On the contrary, if A is negative, the first term of the denominator tends to nil with ever-increasing time, so that C will gradually approach the value

$$C_\infty = -A.$$

That is, the reaction will never proceed beyond this limit, because the enzyme will be gradually annihilated. This will be the case when the initial concentration of the enzyme is relatively small in comparison to that of the substratum.

If $A = 0$, equation (16) or (17) becomes indeterminate, but then equation (15) becomes formally indentical to that of a reaction of the second order, in which both reacting substances are in equivalent quantities. The integration gives:

$$\frac{1}{C} - \frac{1}{C_0} = k't,$$

or

$$C = \frac{C_0}{1 + k'C_0 t}. \qquad (18)$$

Equations (10) and (11) are exactly of the same form, and E can be exchanged for C, if k′ is exchanged for k. Hence we can at once write down the equations which, corresponding to (17) and (18) describe the change of E with time. These equations are:

$$E = \frac{kA' E_0}{\begin{array}{c} kA't \\ k'C_0 l \qquad -kE_0 \end{array}}, \qquad (17')$$

where

$$A' = \frac{k'}{k} C_0 - E_0,$$

and

$$E = \frac{E_0}{1 + k E_0 t}. \qquad (18')$$

A′ has the sign opposite to that of A. Hence in the case where the main reaction proceeds to the end, some of the enzyme remain still active even after a very long time. The limiting value is:

$$E_\infty = -A'$$

If $A=0$, both the substratum and the enzyme tend towards nil with increasing t.

In order to estimate the effect of temperature on the course of the reaction, we must know its influence upon k′. This can also be expressed by an equation similar to (8):

$$k' = e^{\beta\left(\frac{1}{\pi} - \frac{1}{T}\right)}, \qquad (19)$$

where π is the temperature at which k′ becomes equal to unity. The coefficient β will be generally greater than α, so that the ratio $\frac{k}{k'}$ will decrease with rising temperature. Hence, according to equation (12), the velocity of decay of the enzyme must increase more rapidly than the velocity of the main reaction, on elevation of the temperature. The effect of this displacement upon the course of the reaction is perfectly clear because it is equivalent to a greater increase of C_0 in comparison to that of E_0. At a higher temperature the initial velocity will be greater, but it will decrease more rapidly. In the case where the reaction approximates to that of the first order at a lower temperature, it will deviate more and more from the type as the temperature rises. This is what Senter found in the case of catalase obtained from blood.

Putting in equation (18) the values of k and k′ given in (8) and (19), we have:

$$C = \frac{e^{\beta\left(\frac{1}{\pi} - \frac{1}{T}\right)} \left(E_0 l^{\frac{\beta-\alpha}{T} + \frac{\alpha}{\tau} - \frac{\beta}{\pi}} - C_0\right) C_0}{E_0 e^{\alpha\left(\frac{1}{\tau} - \frac{1}{T}\right) e^{\beta\left(\frac{1}{\pi} - \frac{1}{T}\right)} \left(E_0 e^{\frac{\beta-\alpha}{T} + \frac{\alpha}{\tau} - \frac{\beta}{\pi}} - C_0\right) t} - e^{\beta\left(\frac{1}{\pi} - \frac{1}{T}\right)} C_0} \qquad (20)$$

This is the equation which represents the course of the reaction at different temperatures and under varying initial conditions.

There are four constants in this equation: β, α, π and τ. Of these the last is the standard temperature defined in an appropriate manner. The other three must be evaluated experimentally, and this may be accomplished in the following manner.

Let C_1 and C_2 be the values of C at t_1 and t_2, the latter being so chosen that $t_2 = 2t_1$. Then, from equation (16) we get:

$$C_2C_o(C_1 + A)^2 = C_1^2(C_2 + A)(C_o + A).$$

Solving this equation for A, we have:

$$A = \frac{2C_oC_1C_2 - C_1^2(C_o + C_2)}{C_1^2 - C_oC_2},$$

or

$$A = 0.$$

Putting the former value of A in (16) we can calculate k′ from the experimental data. From the values of k′ at different temperatures β and π can be evaluated. Equation (14) then enables us to find the values of k at different temperatures, and from these α can be deduced.

Mr. E. Yamasaki has studied with utmost care the course of decomposition of hydrogen peroxide by catalase obtained from young shoots of bamboos, Phyllotachys mitis, Riv. His results confirm the foregoing deductions in a most remarkable manner, and equation (20), in a somewhat modified form, has been found quite adequate to represent a tolerably large mass of experimental data. His method of evaluating the constants differs somewhat from the one given above and is perhaps better suited for the purpose.

Let us now turn our attention to the case, in which the effect of the substratum and the product of its transformation as well as the effect of the co-existing substances upon the rate of decay of the enzyme remain practically constant through the whole course of the reaction, and consider the interesting problem of the so-called optimum temperature. Equation (4) takes now the simple form:

$$E = \psi(T, t)$$

This relation has often been the subject of study and the equation

$$E = E_0 e^{-e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}t} \qquad (21)$$

has been found to hold in a great many cases. The experiments were indeed mostly performed in the absence of the substrata. It is probable that the presence of the latter would modify the value of β, because many substrata are known to exercise a protective action upon the enzymes; but the form of the equation will not be modified thereby.

When the reaction is one of the first order with respect to the concentration of the substratum, then the velocity is represented by the equation:

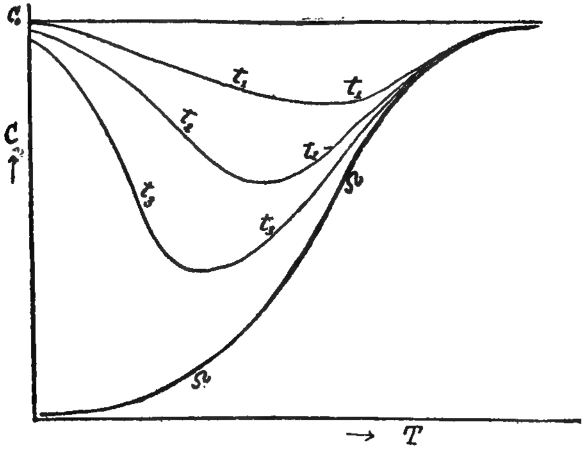
$$\frac{dC}{dt} = -E_0 e^{\alpha\left(\frac{1}{\tau}-\frac{1}{T}\right)} e^{-e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}t} C,$$

which, on integration, gives:

$$\ln\frac{C_0}{C} = -E_0 e^{\alpha\left(\frac{1}{\tau}-\frac{1}{T}\right)-\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}\left(1-e^{-e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)}t}\right) \qquad (22)$$

This is essentially the equation first given by *Tammann*.

As it has been repeatedly pointed out, the notion of the optimum temperature has a definite meaning only when the time interval is fixed, during which the enzymatic action takes place. A graphical representation of equation (22), in which definite values are assigned to t, will make the meaning of the optimum temperature quite clear. In the equation there are three variables, C, T and t. But, when the value of the last is fixed, we have a relation between C and T, which can be represented by a curve. In the annexed diagram the curves for different values of t are shown. Ω Ω is the curve for $t=\infty$. This curve represents



the fact that at a high temperature the enzyme is destroyed so rapidly that the reaction proceeds only a little way and then stops. At a lower temperature the reaction proceeds further before the enzyme is completely annihilated. This is evidently the limiting curve and the curves for limited duration must all lie above it, and indeed the higher as the time allowed is the shorter. The minimum points of the curves represent the temperatures at which the reaction proceeds the furthest in the given intervals. From the figure, we see that the optimum temperature is the higher as the duration of the reaction is the shorter. This relation can be more precisely deduced in the following manner.

Differentiating equation (22) with respect to T, t being assumed to remain constant, we get:

$$\frac{1}{E_0}\,\frac{d\ln C}{dT} =$$

$$e^{\frac{\alpha}{\tau}-\frac{\beta}{\pi}\frac{\alpha-\beta}{T}}\left\{\left(\frac{\alpha-\beta}{T^2}+\frac{\beta}{T^2}e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)t}\right)e^{-e^{\left(\beta\frac{1}{\pi}-\frac{1}{T}\right)t}}+\frac{\alpha-\beta}{T^2}\right]$$

For the optimum temperature the right side of this equation must vanish. Hence,

$$\left(\alpha-\beta+\beta e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)t}\right)e^{-e^{\beta\left(\frac{1}{\pi}-\frac{1}{T}\right)t}}+\alpha-\beta=0.$$

On taking the logarithm and transforming, we get

$$\left(e^{-\frac{\beta}{T}}t\right)=e^{-\frac{\beta}{\pi}}\ln\frac{\beta e^{\frac{\beta}{\pi}}\left(e^{-\frac{\beta}{T}}t\right)+\alpha-\beta}{\beta-\alpha}.$$

Now it is clear that this equation will be satisfied by a definite value of the term in brackets. Let this value be e^h, then

$$e^{-\frac{\beta}{T}}t=e^h,$$

or

$$\frac{\beta}{T}=\ln t-h. \qquad (23)$$

In order to eliminate h, let Θ be the optimum temperature for $t=1$. Then from the foregoing equation,

$$T=\frac{\beta}{\Theta\ln t+\beta}\Theta$$

and

$$\Theta=\frac{\beta}{\beta-T\ln t}T.$$

If Θ is determined under constant conditions well defined with respect to the coexistent substances, etc., it may be regarded as one of the characteristics of the enzyme. But for the purpose of characterization β is evidently more suitable than Θ. If T_1 and T_2 are the optimum temperatures for the durations t_1 and t_2 respectively, then we get from (23)

$$\beta=\frac{\ln t_1-\ln t_2}{\frac{1}{T_1}-\frac{1}{T_2}}.$$

In this way the value of β can be determined in presence of the substratum, and this is most probably of greater practical significance than the value of β measured in its absence, as it is usually the case.

The problem of the maximum temperature is completely covered by equation (22) as far as the decay of the enzyme can be considered as a reaction of the first order, and does not present any feature of theoretical interest.

SUMMARY

Some problems regarding the decay of the enzyme in the presence of the substratum have been investigated. The particular case, in which the velocity of destruction of the enzyme is proportional to that of the transformation of the substratum, has been discussed in detail and several interesting consequences have been deduced. These have received full confirmation from the experimental studies on catalase by Yamasaki. Then the problem of the optimum temperature has been treated, and the relation between this temperature and the temperature coefficient of the decay of the enzyme has been elucidated.

Abstract

CAOUTCHOUK-BENZENE (C_6H_6)—WATER

By W. P. A. Jonker
Goes, Holland

The benzene solution of caoutchouk gives a partial dismixing with water. The system is reversible, therefore the phase rule can be applied. Three liquid layers are formed, of which the concentration was fixed at 30° C.

THE MELTING POINTS OF FIRE BRICKS

By C. W. Kanolt
Bureau of Standards, Washington, D. C.

We are accustomed to thinking of a melting point as a temperature at which a substance changes from a condition in which it does not flow perceptibly under its own weight to a condition in which it flows readily. However, no rational definition of the melting point can be based upon this conception. For example, when glass is heated, the transition from its ordinary condition to a distinctly fluid condition is a very gradual one and occupies a range of several hundred degrees. Some other substances which possess perfectly definite temperatures of transition to a fluid phase, undergo changes resembling fusion at lower temperatures. Solids in general become softer when heated; they may become so soft as to yield to their own surface tension, with the result that sharp corners are rounded off. Rutile, in its natural, slightly impure condition, melts at about 1700° C. The melting point is very definite, there being a sharp transition from a rather soft solid to a liquid of low viscosity, with a considerable absorption of heat. Yet at temperatures 100 degrees or more below the melting point, corners are rounded off and small particles become sintered together. The sintering of clay is probably a similar phenomenon of surface tension. Clay exists generally in the form of extremely fine particles, its unusually slight solubility in water accounting for this condition. Fine particles are more readily united by surface tension than large ones.

A melting point can be precisely and rationally defined only as the temperature at which a crystalline or amisotropic phase and an amorphous or isotropic phase of the same composition can exist in contact in equilibrium. In harmony with this, one might define a solid as a crystalline substance, and a fluid as a substance not crystalline; however, these definitions of solid and fluid would lead to results quite different from our ordinary conceptions, as they would require us to consider glass, even silica glass, as a fluid, and certain "anisotropic liquids" whose viscosities are even less than that of water, as solids. Perhaps it is better to leave solid and liquid or fluid as general terms without precise definitions.

While the above definition of melting point is satisfactory for the case of a pure substance, so complex a mixture as an ordinary fire brick usually has no single definite melting point according to this definition, since several anisotropic phases may be present, all differing in composition from the isotropic phase produced by fusion. We can then only select the temperature at which the transition from a rigid to a fluid state seems most distinct, and can call this the melting point only by apology.

In the case of fire bricks, the transition temperatures so found are fortunately sufficiently definite to make their determination of practical value. I have taken as the melting point the lowest temperature at which a small piece of the brick could be distinctly seen to flow. Experiments showing the degree of definiteness of this temperature will be described.

The melting point of a brick is, of course, not the only property to be considered in determining its fitness for a given purpose. Its crushing strength cold, its behavior under load conditions when heated, and its resistance to fluxes may all be important. The present paper deals only with melting points.

A large number of the brick samples tested were kindly furnished by Dr. A. V. Bleininger, being identical with samples tested by Bleininger and Brown[1] under load conditions at 1300° C., this work being carried out at the Pittsburgh Testing Station of this bureau, which station was at that time the Technologic Branch of the United States Geological Survey. The chemical composition, crushing strength cold, porosity and density of these samples are given by Bleininger and Brown. They also determined the Seger cone numbers corresponding to the softening temperatures of the bricks.[2]

---

[1] Bureau of Standards Technologic Paper No. 7 (1912).

[2] See also: Hofman and Demond, Trans. Am. Inst. Mining Eng. *24*, p. 42 (1894); Hofman, Trans. Am. Inst. Mining Eng., *25*, p. 3 (1895), *28*, p. 435 (1898); Hofman and Stroughton, Trans. Am. Inst. Mining Eng., *28*, p. 440 (1898); Gary, Mitt. k. tech. Versuchsanstalten *14*, p. 63 (1896); Jochum, Thonindustrie Zeit., *27*, p. 764 (1903); Weber, Trans. Am. Inst. Mining Eng. *35*, p. 637 (1904).

It is difficult to interpret results obtained with Seger cones in terms of actual temperatures, for it has been shown by Simonis[1] that the falling over of Seger cones, of certain numbers at least, depends not only upon the temperature, but also to a large extent upon the rate of heating. This observation has been confirmed in this laboratory, using the cone numbers having softening temperatures in the same range as fire brick, and it has appeared that in many cases the melting point of a fire brick, defined as stated above, is more definite than the softening temperature of the corresponding Seger cone. It has, therefore, appeared preferable to use a more direct and more accurate method of determining temperatures.

The experiments were conducted in an Arsem graphite resistance vacuum furnace[2] (Fig. 1). In some preliminary experiments upon fire bricks, samples were heated in graphite crucibles, and exposed to such gases as might remain in the furnace. Although the pressure was kept as low as two millimeters of mercury, there was still a slight reducing action upon the brick, and some samples were blackened superficially. Subsequent work has shown that the action was insufficient to produce any very great difference in the results, but, as a matter of precaution, the specimens were protected by a refractory tube (A, Fig. 1) being placed upon a bed of white alundum (fused alumina) in the bottom of the tube. This tube was supported by the brass collar, B, in which it was made to fit tightly by winding with asbestos string, or otherwise, and which was soldered to the lead gasket by which the joint C in the top of the furnace was made air tight.

The refractory tubes were made of a mixture of 72% kaolin and 28% alumina, these being the proportions for the formation of sillimanite, Al_2O_3,SiO_2. According to Shepherd and Rankin[3] pure sillimanite melts at 1811°. The sillimanite tubes were found to melt at about this temperature. Kaolin tubes were used for some samples of relatively low melting points. Either sillimanite or kaolin tubes were used with all fire bricks melting below 1800°. The chromite and magnesia bricks were melted in graphite crucibles without protecting tubes. The experiments were made rapidly and the graphite had little action on the samples until after fusion had occurred and the melting point had been determined. Magnesia tubes may be used in place of sillimanite tubes, and they have the advantage of a higher melting point, but all magnesia tubes that have been tried have been found to be very easily cracked by changes of temperature, and to be so porous as to afford little protection from the gases of the furnace. When a sillimanite or kaolin tube was used, twenty to thirty minutes was consumed in heating the furnace to a little below the melting point of the sample. This initial heating could be preformed much more quickly, so far as the furnace is concerned, but more rapid heating would be likely to crack the tube. When the temperature had nearly reached the melting point it was raised much more slowly. When these protecting tubes were used, the samples showed only very slight signs of reduction. In certain experiments made with this apparatus, for example the determination of the melting point of platinum as a check upon the work, it has been desirable to still further diminish the chances of the presence of reducing gases. This has been accomplished by the device shown at D in Fig. 1, which consists of a glass tube drawn out into a fine capillary and leading into the furnace. An outer brass tube protects the capillary. This capillary admits a slow current of air to the inside of the refractory tube, and the air passes out through the pores of the tube into the interior of the furnace. By working the vacuum pump continually the pressure in the furnace was kept down to a few millimeters of mercury, in spite of the influx of air. This process was, of course, injurious to the graphite heater, but several such experiments could be made with one heater before it was burned out.

---

[1] Simonis, Tonisdustrie Zeit. *32*, p. 1764 (1908).

[2] Arsem, Jour. Am. Chem. Soc., *28*, p. 921 (1906); Trans. Am. Electroch. Soc., *9*, p. 153 (1906).

[3] Shepherd and Rankin, Am. Jour. Sci., *28*, p. 301 (1909).

While the sample was being heated it was observed through the window E at the top of the furnace. A glass window was used here in place of the mica window provided by the makers of the furnace. The glass was attached by a mixture of rosin and beeswax. To keep this material cool an additional water jacket, F, was applied to the part of the furnace projecting above the water of the tank.

The temperatures were determined by means of a Morse optical pyrometer of the Holborn-Kurlbaum type,[1] which was sighted vertically downward through the furnace window. The current in the pyrometer lamp was measured with a Siemens and Halske milliammeter with a shunt. This instrument was calibrated several times, and its very small temperature coefficient was taken into account. Its readings are certainly reliable to .001 ampere and probably to .0005 ampere.

The carbon-filament pyrometer lamp was one of the standard lamps of the bureau, and had been thoroughly aged, and had been accurately calibrated by several observers before the beginning of the investigation, and again, by a different method, toward its close. In the first calibration it was sighted into a platinum resistance furnace in which black body conditions were obtained, and the temperature of which was measured by platinum, platinum-rhodium thermocouples. These thermocouples had been calibrated against the freezing points of pure metals. In the second calibration the lamp was calibrated against the freezing points of metals directly, without the intermediation of thermocouples. The metals used were copper, silver, and the copper-silver eutectic, which freeze at 1083°, 961°, and 779° respectively. These were placed in Acheson graphite crucibles of the form shown in Fig. 2, about 100 grams of metal being used in each. The pyrometer was sighted downward into the central graphite tube, of which the inside diameter was 6 mm and the wall thickness 1 mm. The crucibles were heated or cooled gradually, while observations were made every ten to twenty seconds, and the resulting heating or cooling curves were plotted. A typical curve is shown in Fig. 3. In this diagram, a change of temperature of 1° corresponds to a change of current of about .0005 ampere. By means of the three known temperatures, the relation between the current in the lamp and the temperature was expressed in the form, $C = a + bt + ct^2$.

This method presented two possible sources of error to be especially considered, namely, the conduction of heat along the inner graphite tube, and the departure of the interior of this tube from black-body conditions. If the conduction of heat along the tube introduced appreciable error, the observed temperatures would be too high with rising temperature, when the furnace heater would be hotter than the metal, and too low with falling temperature, when the reverse would be true. The fact that the results from the heating curves obtained with copper and silver were in very close agreement with those from the cooling curves shows that the errors from conduction are negligible; and these and numerous other observations have indicated that such a tube when made of graphite, which is itself nearly perfectly black, is a very good black body. Using the copper-silver eutectic somewhat unsatisfactory results were obtained with heating curves, the trouble appearing to be in the behavior of the alloy rather than in the temperature measurement. In this case only cooling curves were used for the calibration. The calibration of the lamp at this temperature is relatively unimportant, since none of the melting points here given correspond to a lamp temperature below the melting point of silver. The results of this calibration agreed with those obtained by the first method within one degree from 700° to 1300°, which includes all lamp temperatures used in this work. Near the close of the investigation the pyrometer lamp was accidentally overheated, and it was necessary to recalibrate it. This time, only the cooling curve method was used.

---

[1] Holborn and Kurlbaum, Sitzber. d. k. Akad. d. Wissensch. zu Berlin, June 13, p. 712 (1901); Ann. der Phys., *10*, p. 225 (1902); Waidner and Burgess, Bull. Bureau of Standards, *1*, No. 2 (1904); Mendenhall, Phys. Rev., *33*, p. 74 (1911); Henning, Zeit. f. Instrumentenkunde *30*, p. 61 (1910).

As the melting points to be measured were above the working limit of the pyrometer lamp, an absorption glass was interposed between the pyrometer and the furnace. This glass was calibrated as follows. In the Arsem furnace was placed a graphite crucible, the interior of which, when the furnace was hot, furnished a field of very uniform brightness. A steady current was passed through the furnace and the temperature allowed to become stationary. The temperature was then measured with the pyrometer, and also the apparent temperature as observed through the absorption glass. If T_1 is the absolute temperature, observed without the glass, and T_2 is the apparent absolute temperature observed with the glass, we have the following relation, which is easily deduced from the Wien radiation law,

$$\frac{1}{T_2} - \frac{1}{T_1} = A$$

The constant, A, was determined in this way with several different furnace temperatures, and the results were in close agreement. The mean value of A was .0002249. The values of the constants of Wien's law do not enter into the work.

The glass furnace window absorbed and reflected a small amount of light and it was necessary to apply a correction for this. The constant of this glass was determined in the same way as that of the absorption glass, and was found to be .0000040. The correction in degrees depends of course upon the temperature; it is about 15° at the melting point of ordinary fire brick.

As a check upon the whole apparatus, a determination of the melting point of platinum was made. A piece of platinum foil was placed within two magnesia tubes, one within the other, in the place of the single tube shown at A (Fig. 1), and a slow current of air was admitted at D. Fairly good black body conditions were obtained but the platinum was faintly visible. The observed melting point was 1750°. The value accepted by the Bureau of Standards as the melting point of platinum is 1755°. After the pyrometer lamp had been overheated and recalibrated, this test was repeated. In place of magnesia tubes, tubes of a mixture of magnesia and alumina,[1] obtained from the Königliche Porzellan-Manufactur, Berlin, were used. These were found to be more satisfactory than magnesia tubes, being much less porous and less easily cracked. The material softens at a little above the platinum point. Using a single tube the value 1746° was obtained, with two tubes 1750°. Tests were also made in an iridium tube furnace where there was no possibility of a reducing atmosphere. So good black body conditions were obtained that the platinum was quite invisible. A piece heated to 1747° and removed was found not melted; one heated to 1759° and removed was found melted.

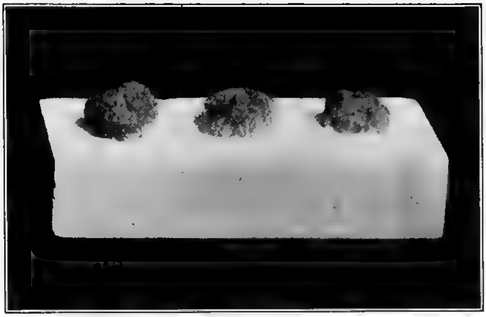
The use of the optical pyrometer depends upon the assumption that the object sighted upon emits black-body radiation. This is the case if the object is within a vessel at uniform temperature, and is viewed through a relatively small opening in the vessel.

[1] Heinecke, Zeit. angew. Ch., *21*, p. 687 (1908).

This can readily be accomplished in the apparatus used, but under such conditions it would be impossible to distinguish the sample, owing to the uniform brightness of the sample and its environs. In practice, the sample was placed slightly below the hottest part of the furnace, in such a position as to be barely distinguishable. This requires only a temperature difference of about five degrees. When the temperature of a sample had almost reached the melting point, the temperature was raised more slowly and the sample was observed continually. When it was seen to melt, a final temperature measurement was made and the heating current was immediately stopped, thus preventing the temperature from rising any higher. The observation was then verified by an examination of the sample after its removal from the furnace.

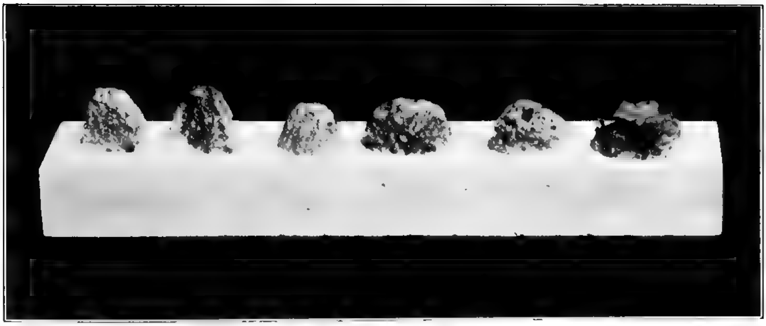
An idea of the degree of definiteness of the melting points may be obtained from Fig. 4 and Fig. 5, in which are shown samples which have been heated to successively higher temperatures. Fig. 4 may be taken to represent the usual degree of definiteness. The sample heated to 1680°C. appears unaffected; that heated to 1695° shows very slight signs of fusion; that heated to 1705° is completely fused. 1705° was taken as the melting point. Fig. 5 shows perhaps the least definite melting point found. Complete fusion occurred at 1620°, but there was partial fusion at considerably lower temperatures, 1600° was taken as the melting point.

Near the melting point, samples were heated at the rate of about ten degrees per minute. This rate of heating was quite slow enough, as a temperature measurement can be made in a few seconds and a slower rate of heating near the melting point was found to give the same results. The entire time required for heating a sample from room temperature to its melting point was thirty to forty minutes. Experiments were made to determine whether samples could undergo any change in melting point as the result of heating in the vacuum furnace. Samples of various kinds were heated in the furnace to about 1550° for about six hours, and their melting points were then determined. The results are given in Table I.



1680° 1695° 1705°

Figure 4



1570° 1580° 1590° 1600° 1610° 1620°

Figure 5

TABLE I

Sample Number	Material	Determinations of melting point without previous heating	Determinations of melting point after six hours heating
14	Fire clay	1635°	1655°
		1630°	1655°
27	Fire clay	1600°	1635°
		1610	1630
		1600	1635
		1585	1640
		1595	
48	Fire clay	1710°	1705°
		1705	1695
		1705	
		1700	
		1705	
20	Bauxite	1740°	1740°
		1745	1730
41	Silica	1705°	1695°
		1700	1700
		1695	
		1695	

It appears from the table that Nos. 14 and 27, which are bricks of low melting point, melted at a somewhat higher temperature after long heating; while the other bricks were unaffected. The melting point of No. 27 is less definite than that of most bricks. This increase of melting point might be accounted for upon the assumption that the brick consisted of two materials existing in distinct particles, one sort having a lower melting point than the other, these two materials becoming run together after long heating near the melting point, producing a material of higher melting point than that of the more fusible of the original materials. The appearance of samples of No. 14 and No. 27 after heating for a short time to near the melting point supports this explanation. Sample No. 27 is shown in Fig. 5. After the six hours heating they appeared more uniform. Long heating in a vacuum would tend to vaporize the more volatile constituents of the brick, and this might produce an appreciable increase of melting point.

The most common fire brick are those made of clay, of which the essential ingredient is kaolin, $Al_2O_3,2SiO_2,2H_2O$. Shepherd and Rankin[1] found that the only compound of alumina and silica that can exist in the neighborhood of the melting points is sillimanite, Al_2O_3,SiO_2. It follows that clay when near its melting point is no longer a single compound but a mixture of Al_2O_3,SiO_2 and SiO_2. Hence the melting point of pure kaolin, like that of fire brick, can not be expected upon theoretical grounds to be perfectly definite, but fairly definite results are obtained when the visible flow is taken as the criterion of fusion, as in the case of fire brick. Two samples of white kaolin, one English, the other probably English also, both melted at 1740°. A sample of brownish white German kaolin melted at 1735°. Therefore the highest melting point that can be attained in brick containing nothing more refractory than kaolin is 1740°. When an excess of alumina is present, as in bauxite brick, the melting point may be higher.

A few brands of silica brick were tested. Pure silica melts at about 1600°.[2] However, the fused silica possesses such extreme viscosity near the melting point that it does not flow or change shape distinctly until considerably higher temperatures are reached. I have obtained 1750° as the *apparent* melting point of pure silica, *i.e.*, the temperature at which it flows distinctly. This temperature, however, is naturally a very indefinite one. The temperature at which silica bricks flow distinctly is more definite.

Bauxite brick are made from bauxite, $Al_2O(OH)_4$ containing usually considerable quantities of other material. Bauxite, of course, becomes converted to alumina, Al_2O_3, when heated. Pure alumina melts at about 2010°.[3] None of the bauxite bricks examined approached this melting point. A single sample of bauxite was tested and found to melt completely at 1820°, the center of the nodules melting at 1790°. A sample of bauxite clay melted at 1795°.

One brand of magnesia brick was examined and found to melt at 2165°. The melting point of pure magnesia is more or less in doubt at present. It is certainly much higher than that of the impure magnesia brick. This brick contained a large quantity of iron and was of a dark brown color. When heated for a few minutes to near its melting point it became white. This occurred both in the electric vacuum furnace and in an oxy-hydrogen flame. It might result either from the vaporization of the iron, or from the formation of a colorless compound of iron and magnesia. An analysis of the specimens has shown that the heated samples contain much less iron.

---

[1] Loc. cit.

[2] Day and Shepherd, *Jour. Am. Chem. Soc.*, *28*, p. 1089 (1906).

[3] A paper on the melting points of pure refractory oxides is in preparation.

One brand of brick made from chromite, FeO,Cr_2O_3, was examined. It was found to melt at 2050°. A sample of natural chromite from a different source melted at 2180°.

Silicon carbide, SiC, has been used as a refractory material. At very high temperatures it decomposes without melting. Tucker and Lampen[1] state that it decomposes at 2220°. Results in close agreement with this have been obtained by Gillett[2] and by Saunders.[3] This is undoubtedly correct for decomposition under ordinary conditions, but silicon carbide can be heated for a short time to much higher temperatures without complete decomposition. It was thought that by very rapid heating it might be possible to reach the melting point of the silicon carbide before decomposition was complete, although such a melting point would probably have only theoretical interest. With this object, a few grams of silicon carbide was placed in a graphite crucible, which was placed in a second larger graphite crucible to give more uniform temperature and the whole was heated in an arc furnace at atmospheric pressure, the temperature being measured by sighting the optical pyrometer through a narrow graphite tube inserted in the top of the crucible. A temperature of 2700° or more was reached and was maintained for a few minutes. The silicon carbide was about half decomposed, leaving a residue of carbon, but showed no indication of fusion.

The results for fire brick will be found in Table II. Samples 1 to 26 are identical with the samples of the same numbers studied by Bleininger and Brown.[4] All the bricks tested were made in the United States. Each melting point given is the mean of at least two determinations. The mean of the melting points of the 41 samples of fire clay bricks is 1649°.

---

[1] Tucker and Lampen, *Jour. Am. Chem. Soc.*, *28*, p. 853 (1906).
[2] Gillett, Jour. Phys. Chem., *15*, p. 213 (1911).
[3] Paper presented before the American Electrochemical Society, May, 1912.
[4] Loc. cit.

TABLE II

FIRE CLAY BRICK

Sample Number	Melting Point	Sample Number	Melting Point
1	1630	26	1695
2	1635	27	1600
3	1605	28	1695
4	1605	29	1595
5	1705	30	1560
6	1705	31	1600
7	1700	32	1650
8	1700	33	1655
9	1675	34	1570
10	1710	35	1650
11	1660	36	1590
12	1555	37	1650
13	1635	38	1660
14	1630	47	1725
15	1655	48	1705
17	1650	49	1715
21	1615	53[1]	1635
22	1640	54[1]	1635
23	1660	55[1]	1685
24	1660	56[1]	1605
25	1715		

BAUXITE BRICK

Sample Number	Melting point
19	1760
20	1740
44	1720
45	1785
46	1720
50	1665
51	1565
52	1590

[1] Samples 53, 54, 55 and 56 are of the same brands as 4, 9, 7 and 17 respectively, but from different lots.

SILICA BRICK

Sample Number	Melting point
39	1700
40	1705
41	1700

CHROMITE BRICK

Sample Number	Melting point
42	2050

MAGNESIA BRICK

Sample Number	Melting point
43	2165

The analyses of a large number of the fire clay bricks studied are available,[1] but it does not seem possible to establish any very definite relation between composition and melting point. Since the bricks contain about eight different constituents in quantities sufficient to affect the melting point, and since the melting point may also be affected by lack of homogeneity in the material, it is obvious that a prediction of the melting point upon the basis of a chemical analysis would be uncertain. If the melting points are compared with the results of tests under load conditions at 1300°,[2] it is evident that there is little relation between the two.

SUMMARY

1. The melting points of 54 samples of fire brick, including fire clay, bauxite, silica, magnesia, and chromite brick, have been determined in an electric vacuum furnace, the temperature being measured with an optical pyrometer (Table II).

2. The following melting points of materials important in the manufacture of fire brick were determined:

---

[1] Bleininger and Brown, loc. cit.
[2] Bleininger and Brown, loc. cit.

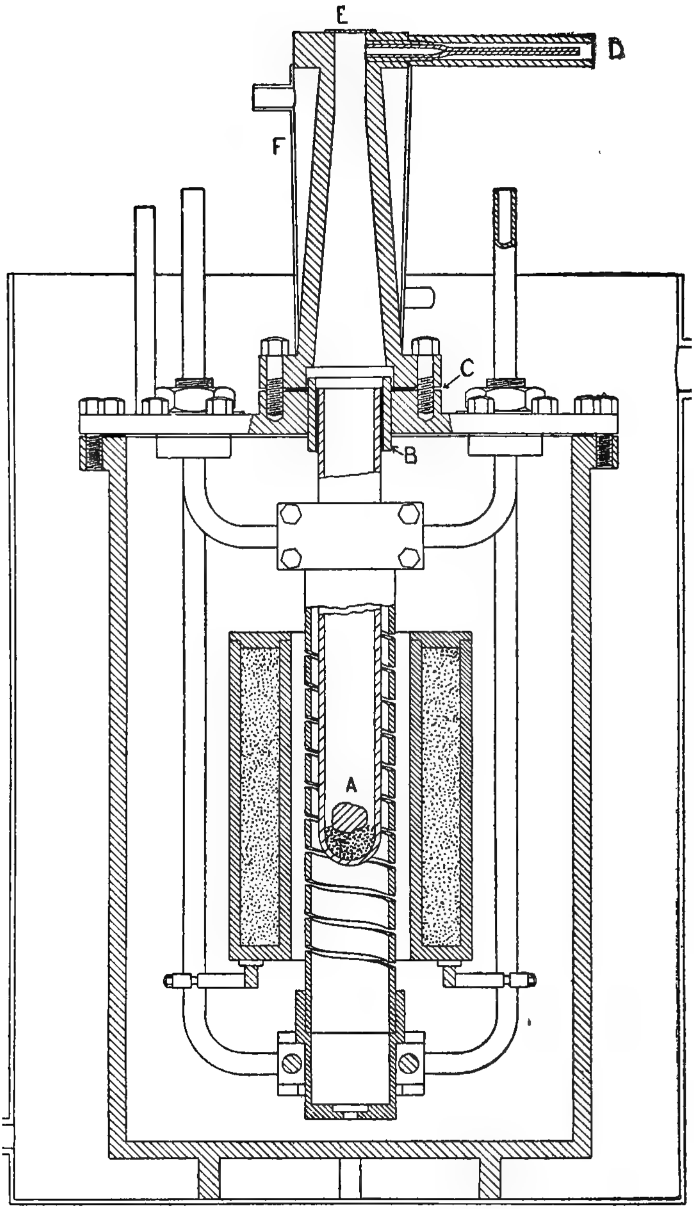


FIGURE 1

Kaolin	1740°
Pure alumina	2010°
Pure silica	1750°[1]
Bauxite	1820°
Bauxite clay	1795°
Chromite	2180°

3. An improved method of calibrating the Holborn-Kurlbaum optical pyrometer is described.

Mr. H. P. Greenwald and Mr. S. E. Moore have rendered efficient assistance in carrying out this work.

---

[1] This is not the true melting point but represents approximately the temperature at which silica flows distinctly.

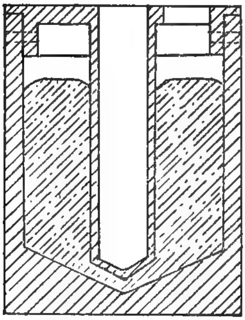


Figure 2.

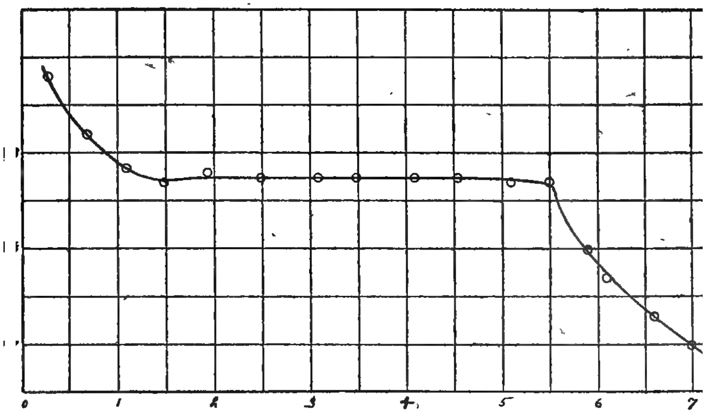


Figure 3.

ON THE PRESENT THEORY OF MAGNETISM AND THE PERIODIC SYSTEM OF CHEMICAL ELEMENTS

By Jakob Kunz

Assistant Professor, University of Illinois, Urbana, Ill.

This paper contains the following topics:

1. Fundamental assumptions.
2. Experimental facts; diamagnetism, additive and non-additive properties.
3. The periodic system of the elements and their magnetic properties.
4. Ferromagnetism.
5. The magneton of Weiss and the degrees of freedom.

I

FUNDAMENTAL ASSUMPTIONS

The electron theory seems to account for the magnetic phenomena in a very direct way. Indeed, we have only to assume that the molecular currents of Ampère, which form the elementary magnets, are revolving electrons, in order to express Ampère's theory of magnetism in terms of the electron theory. A closer study of the electronic orbits, however, due to Voigt and J. J. Thomson, showed that these currents cannot account sufficiently for the phenomena of diamagnetic and paramagnetic bodies. It was only on the basis of the researches of P. Curie, that P. Langevin was able to give a more satisfactory theory of diamagnetism and paramagnetism. Curie found that the diamagnetic susceptibility is independent of the temperature, while the paramagnetic susceptibility is inversely proportional to the absolute temperature. Langevin concluded, therefore, that there is a fundamental difference between diamagnetic and paramagnetic properties. In Langevin's theory the diamagnetism is a characteristic property of each molecule which contains a certain number of revolving electrons. If the resultant magnetic moment of these electrons in an atom is zero, then the body is diamagnetic; the action of an external magnetic field consists in a change of the orbit, the diamagnetic modification of the atom. If the revolving electrons possess a resultant magnetic moment, the body is paramagnetic. Matter in all its forms is diamagnetic; paramagnetism, whenever it appears, covers, as it were, the diamagnetism without transition between the two distinct groups. Langevin insists that the paramagnetic constants are very large in comparison with the diamagnetic constants. Consider an electron of mass *m* and charge *e* revolving with velocity *v* in an orbit of radius *r*, the plane of which is perpendicular to a magnetic field H, the centifugal force is balanced by an elastic force *f*. Without a magnetic field we have

$$\frac{mv^2}{r} = fr.$$

If the magnetic field acts on the electron its velocity will not be changed, but the radius of the orbit will suffer a change. Let the new radius be r^1, then:

$$\frac{mv^2}{r^1} = fr^1 - Hev$$

and the change of the magnetic moment of N electron per unit volume is equal to:

$$\Delta M = \frac{-He^2Nr^2}{2m} = -kH$$

The diamagnetic susceptibility *k* is therefore equal to:

$$k = \frac{N}{2}\frac{e^2}{m}r^2$$

If now the magnetic moment of all the revolving electrons in the atom in an external point is zero, then the substance is purely diamagnetic and the diamagnetic susceptibility *k* independent of the temperature, if the number of revolving electrons N and the radius of the orbits are not affected by the temperature. If the electronic orbits have a resultant magnetic moment in an external point, then these magnets will be directed by the magnetic field and constitute a paramagnetic body, and both the thermodynamic and kinetic treatment of the problem show that the paramagnetic susceptibility is inversely proportional to the absolute temperature. In addition Curie concluded that a change of physical or chemical state has hardly any influence on the diamagnetic properties.

II

EXPERIMENTAL FACTS

The phenomena are far more complicated than this theory of Langevin indicates. The positive paramagnetic values are on the whole not larger than the negative diamagnetic ones, as is shown by the following table: k is the susceptibility per unit volume,

	$k\ 10^6$		$k\ 10^6$
Pb	−1.37	Al	+1.8
Au	−3.07	Be	+0.29
C (Diamond)	−0.49	B	+4.32
C (amorphous)	−2.02	Mg	+0.57
Hg	−2.6	Na	+2.2
Ag	−1.4	Pd	+5.15
Bi	−13.7	Pt	+29.0
Cd	−1.16	Si	+0.2
Tl	−4.6	N	+0.0537
Cu	−0.82	Mo	2.2
		Os	0.62

Certain elements seem to exist in both the diamagnetic and paramagnetic state. Thus, for hydrogen, I find in Boernstein-Landolts tables: the value +0.008, while Dewar[1] gives a negative value, the magnetic properties of elementary gases and vapors are still insufficiently known. This is, for instance, true for nitrogen. Boron, carbon and silicon seem also to exist in the diamagnetic and paramagnetic state. H. E. Dubois and K. Honda[2] give for crystalline silicon +0.12 and amorphous −0.14. In this respect tin seems to have the most interesting properties. If diamagnetic gray tin is slowly heated, at 32°, k $(= -0.29)$ changes almost suddenly and at 35° passes through zero. Possibly this change would wholly take place at the point of transformation 18°, but then at a much slower rate. Further heating continuously increased k so that at about 50° the value +0.03 for paramagnetic tetragonal tin was reached, which afterwards remained practically constant. At 161° nothing particular was noticed. At the melting point a discontinuity from +0.03 to −0.04 once more appeared; the diamagnetic liquid metal remained nearly unchanged.

---

[1] Rapports du congres international de physique, vol. 2, p. 506 (1900.)

[2] Acad. Weteuschap. Amsterdam Proc. 12, p. 596-602 (1909-10).

The paramagnetic susceptibility is independent of the temperature over an interval of as much as 500° in the following elements: Na, Al, K, V, Cr, Nb, W, Os; the paramagnetic susceptibility increases with increasing temperature for the elements: Ti, V, Cr, Mn, Mo, Ru, Rh, Tr, Th. These are all exceptions from Curie's rule; it seems to me not justified, to maintain this rule, as there are many more exceptions than confirmations. The same is true for the diamagnetism. Here in a few cases the susceptibility increases with increasing temperature, while for the following elements the diamagnetic susceptibility decreases with increasing temperature: C(amorphous), Cu, Zn, Zr, Cd, Jn, Sb, Te, J, Tl, Pb, Bi (0−268). There are only very few elements which do not vary within the whole temperature range. The starting point of Langevin's theory is undermined. If we consider the magnetic properties of the elements in the periodic system, we find a certain periodic change of the diamagnetic and paramagnetic properties. A very striking exception is given by oxygen, which is strongly paramagnetic; but if oxygen combines with the paramagnetic elements Be, Mg, Al, Mo, W, Th, it forms diamagnetic oxides. The oxides of metals in general are very interesting in this respect, for instance, FeO is weakly magnetic, Fe_2O_3 is stronger and Fe_3O_4 is very strongly magnetic. A strongly magnetic oxide is also Cr_5O_9. At all events, the diamagnetism is a largely non-additive property in inorganic compounds; and the magnetic properties depend so much on chemical and physical influences that one might be inclined to ascribe them to electrons, which are revolving on the surface of the atom. In organic compounds, however, it has been shown by P. Pascal that the molecular susceptibility χ_m is an additive property of the atomic susceptibility χ_a, such that

$$\chi_a = \Sigma a \chi_a + \lambda$$

where λ is a correcting term depending on the structure of the compound being= in the saturated compounds, but amounting to over 6% in certain nonsaturated groups. Oxygen plays in these compounds a very interesting role. Bound up with two different atoms, $-CH_3C_2HOH-$ it is diamagnetic, its atomic susceptibility being -48.10^{-7}. Oxygen by two bonds connected with one carbon atom is still diamagnetic, if this carbon atom—$CH_3CO\,OH$—is connected with a second oxygen atom, the atomic susceptibility is

-35.10^{-7}. Oxygen—CH_3COCH_3—with a double bond connected with C, which carried no other O, is paramagnetic, and its magnetic susceptibility is $+18.10^{-7}$. In more complicated compounds, however, the structure has a great influence on χ. For two groups, the halogenes and intriles, exceptions have been found to the rule of additivity.

III

THE PERIODIC SYSTEM OF THE ELEMENTS AND THEIR MAGNETIC PROPERTIES

The elements may be arranged in series according to the atomic weights in different ways. A certain periodicity between atomic weights and magnetic properties always appears. But if the atomic weights are represented by abscissæ and the magnetic susceptibilities as ordinates, the curve obtained is of a most irregular character, representing seven distinct maxima, among which that of the iron group is by far predominating. If only the sign of the magnetic properties is taken into account, one gets the best representation perhaps by the method of the helix due to B. K. Emerson, which is given in Fig. 1.

The strongly magnetic groups appear on a diameter, where we find Fe, Ni, Co, then Pd, Ru, Rh, then Gd, En, Sm, then Pt, Ir, Os. Moving on the spiral from iron to the right, we meet Mn and Cr, elements, which are paramagnetic, but whose strongly magnetic properties appear only in some of their alloys and compounds such as the Heusler alloys, mangenese-antimony, manganese-tin, manganese-zinc, Cr_5O_9. On the right-hand side from the ferromagnetic elements there are the paramagnetic elements; on the left-hand side, the diamagnetic elements. Opposite to the magnetic metals there are the inert gases, whose magnetic properties have not yet been determined. On the right-hand side of the inert gases we find the alkali metals, whose magnetic properties are not yet sufficiently known. Sodium and potassium seem to be paramagnetic. The strongly magnetic metals, cobalt, nickel and iron, belong to the elements with minimum compressibility, complex volume, with most complex spectra, with complex double salts, with great condensation of mass, the heavy metals. Thus it looks as if the condensation of electronic orbits were a maximum

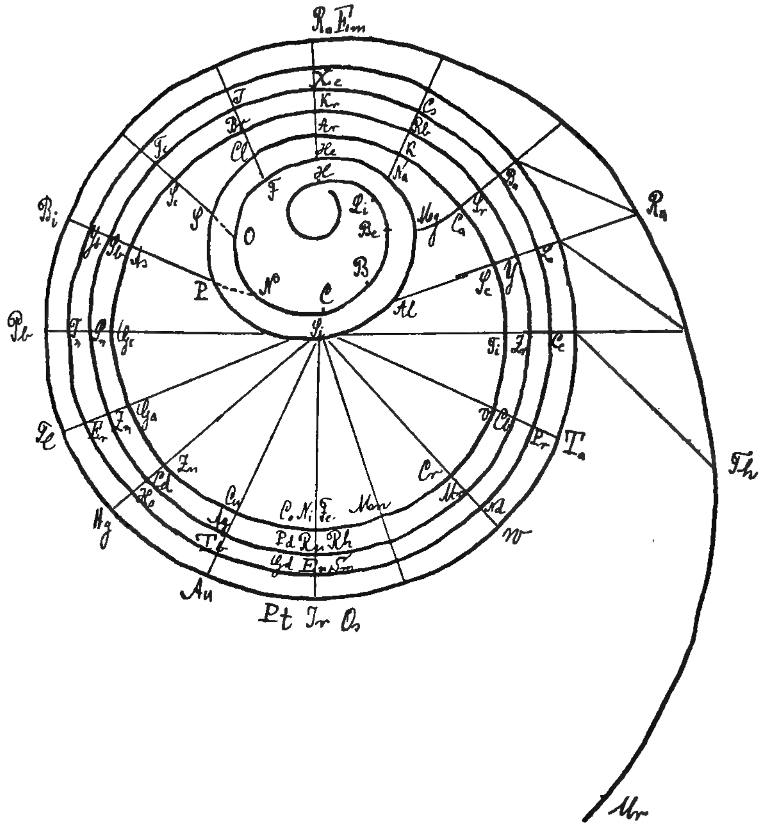


Figure 1

in these magnetic metals, and that the magnetic properties were related directly or indirectly to the mechanical and optical properties. But it is very remarkable that immediately after the strongly magnetic metals there follow the diamagnetic metals:

	k
Cu	-0.66
Ag	-1.4
Tb	. . . . .
Au	-2.6

On the next diameter we have

	k
Zn	-0.96
Cd	-1.16
Ho	......
Hg	-2.6

When we move outward on a diameter of the spiral, the diamagnetic susceptibility increases. The same rule is repeated by chlorine, bromine and iodine; sulphur, selenium, tellure; phosphorous, arsenic, antimony, bismuth. If a represents the atomic weight, α and β two constants, then the atomic susceptibility can be represented for the last three groups by:

$$\chi_a = -C_e^{\beta a - \alpha}$$

The same law seems to hold for all the groups of diamagnetic elements, which are in the previous representation on the left of the diameter passing through the iron group and the inert gases. Thus, for instance, for zinc, cadmium and mercury we have:

$$\chi_{Zn} = \frac{0.96 \times 65.4}{7.1}.10^{-6} = 8.83 \times 10^{-6}$$

$$\chi_{Cd} = \frac{1.16 \times 112.4}{8.6}.10^{-6} = 15.2 \times 10^{-6}$$

$$\chi_{Hg} = \frac{2.6 \times 200 \times 10^{-6}}{13.6} = 38.3. \times 10^{-6}$$

If we put

$$\chi_a = 10^{\beta_a + \beta}$$

where a is the atomic weight, we find from Cd and Hg for α and β the values:

$$\alpha = 0.6146$$
$$\beta = 0.00502$$

log $\chi_{Zn} = 1.583$, the calculated value $= 1.618$. The agreement is not so good for the last diamagnetic group of elements, Cu, Ag and An; here the atomic susceptibilities are as follows:

$$\chi_{Cu} = 5.29 \times 10^{-6}$$
$$\chi_{Ag} = 14.39. \times 10^{-6}$$
$$\chi_{An} = 26.55 \times 10^{-6}$$

The copper seems to make an exception. Whether this is due to an inaccurate determination of χ or to the fact that copper follows immediately after the iron group, remains an open question. Between the Zn, Cd, Hg group and the P, As, Sb group there are two more groups of diamagnetic elements; namely, those of Ga, Jn, Tl, and Ge, Sn, Pb. I find only the values

$$\chi_{Sn} = \frac{0.29\times 119}{5.8} = 5.9 \,.\, 10^{-6}$$

$$\chi_{Pb} = \frac{1.37\times 206.9}{11.37} = 25.0 \,.\, 10^{-6}$$

This agrees also with the general statement that along any diamagnetic diameter of the spiral the atomic susceptibility increases towards the periphery. It is an exponential function of the atomic weight.

If we travel along the spiral from copper towards zinc and from Ag towards Cd, we find the following values for the atomic susceptibilities:

Cu	5.29	10^{-6}	Ag	14.4
Zn	8.83		Cd	15.2
Ga	.....		In	.....
Ge	.....		Sn	5.95
As	5.8		Sb	77.5
Se	24.0		Te	38.9
Br	21.9		I	46.5

As and Sn are two decided exceptions to the rule that the atomic susceptibility increases from the south towards the north of the graphic representation.

While in the strongly magnetic metals the susceptibility decreases as we move on the diameter outward, we see here in the adjacent elements the diamagnetic susceptibility increases when we travel in the same direction. Oxygen again occupies an exceptional position through its magnetic properties. Its regular diamagnetic properties seem to appear only in some of its organic and inorganic compounds. Let us consider the gases:

O_2	CO_2	H_2O	NO	N_2	H_2
+	−	−	+	−	−

The + sign indicates paramagnetism the − sign diamagnetism.

It looks as if in free oxygen one of the atoms were in a different magnetic state than when it occurs in compounds. The same phenomenon occurs, for instance, in the ferricyanides, where the iron seems to have lost its magnetic properties, the ferridyanides being no more magnetic than salts not containing iron; even the combination FeO is very weakly magnetic. There exists a remarkable but very hidden relation between chemical and magnetic properties.

A modification of the theory of the difference between diamagnetic and paramagnetic properties will now be considered.

The phenomena mentioned in the previous paragraph seem to indicate that the magnetism is, as it were, due to revolving electrons on the surface of the atom, and that these electrons are connected with those forces which come into play in chemical reactions, in the optical phenomena and in mechanical properties. There appears to be no special reason why we should ascribe to all matter the diamagnetic rather than the paramagnetic property. Indeed, we may proceed in this way and assume that all matter is paramagnetic, each molecule having revolving electrons, with a resultant magnetic moment for an external point, so that the substance as such is paramagnetic. Let us further assume that there are non-revolving electrons present which, while the external magnetic field is excited begin to revolve and revolve as long as the field lasts. These induced currents constitute the diamagnetic modification of the substance. If the resultant moment of these electrons is larger than that of the previously revolving electrons, then the substance is diamagnetic; if it is smaller than that of the previously revolving electrons, then the substance is paramagnetic. The fact that all substances have a line spectrum and that the lines are subject to the action of the magnetic field is not against this consideration. There is no evidence that the vibrating electrons, which produce the line spectra, are at the same time the revolving electrons of the magnetic properties. If an element like iron is very rich in emission lines then it may also contain a large number of revolving electrons, which produce the magnetic properties. In the elementary theory of the triplet and doublet in the Zeeman effect an electron is considered, vibrating in a given line under a certain angle with the direction of the magnetic field, this vibration is resolved in two components, one of which is parallel and the other perpendicular to the magnetic field; the light emitted in the direction of the lines of force is due to the perpendicular component of the vibration of the electron and consists of two circularly polarized beams. The transversal effect consists in three lines of plane polarized light. Now if we consider the light emitted not from a vibrating, but from an electron revolving in a plane perpendicular to the magnetic field, then we would see in the direction of the lines of force only the original line displaced, and if there be another electron revolving in the opposite direction in the same plane, then we would have the doublet of the longitudinal effect, as if there were only one electron vibrating.

The light emitted by a revolving electron in the transversal effect would be plane polarized, and if there were two electrons revolving in opposite directions, we would have plane polarized light also; and if there were an electron revolving in a circle whose plane coincided with the direction of the field, then its light emitted in the transversal direction would not be affected by the magnetic field, so that we finally have the triplet of the transversal effect. Thus we see that the simple case of the Zeeman effect can be explained either by one vibrating electron or by three revolving electrons. We can, therefore, not conclude that the revolving electrons which produce magnetic effects are at the same time those which are the sources of light. It is possible, but we have no proof as yet. At all events, the fact that the Zeeman effect occurs only in quasi abnormal states of matter as a consequence of ionisation, while the diamagnetism is a normal phenomenon, independent of ionisation, seems to point to the view that different electrons cause the two phenomena.

Let us consider an electron in equilibrium under the action of a system of electrical forces, but able to revolve in an orbit under the electrical forces induced during the establishment of an external field. Let: T be the final time of revolution,

E the electrical force acting on the electron,
e the charge,
m the mass of the electron,
ϕ the magnetic flux crossing the area A of the circle,
r the radius of the orbit,
v the final velocity,
ΔM the increase of the diamagnetic moment per unit volume,
N the number of such orbits per unit volume,

then we have

$$-\frac{d\phi}{dt}=2\pi rEe$$

$$-d\phi=2\pi rEedt;\ mdv=eEdt$$

$$-d\phi=2\pi rmdv$$

$$\phi=2\pi rm\int_{o}^{t}dv=2\pi rmv.=H\pi r^2$$

$$v_1=\frac{Hr}{2m};\ T=\frac{2\pi r}{v_1}=\frac{4\pi m}{H}$$

$$\Delta M=N\Delta m=NAi=NA\frac{e}{T}=\frac{Nr^2eH}{4m}$$

By definition, the diamagnetic susceptibility *k* is given by

$$\Delta M=kH$$

Comparing the last two equations, we have:

$$k=k_2=\frac{Nr^2e}{4m}$$

In the previous theory we had:

$$k_1=\frac{N}{2}\frac{e^2r^2}{m}$$

In the modified theory, therefore, we have to assume that the radii are very small in comparison with what they would be in the older theory, and that N, the number of diamagnetic electrons, is small. In this case the difference between diamagnetic and paramagnetic elements would mainly depend on the kinetic energy of the electrons. If the kinetic energy of rotation is large we have paramagnetic substances; if it is small we have diamagnetic elements.

On the basis given above, P. Langevin worked out the kinetic theory of paramagnetic gases and found that the susceptibility *k* should be inversely proportional to the absolute temperature. This would be the theoretical demonstration of Curie's rule. But Dubois and Honda state that only palladium foil on heating followed more or less Curie's law, and showed complication on cooling. Moreover, Fe, magnetite, nickel, cobalt above the critical temperature seem to follow this simple law. Other ferromagnetic substances, such as phrrhotite above the critical temperature, behave in a very peculiar way. The kinetic theory of the paramagnetic properties can not, without modification, be extended to the liquid and solid state, because here the neighborhood of other atoms and the crystalline structure must have an influence on the magnetic properties of the molecules. This appears very distinctly from the measurement of Dubois and Honda.

IV

FERROMAGNETISM

P. Weiss has shown that the ferromagnetic properties can be described in an exceedingly simple way, namely, by the assumption of an intrinsic or molecular magnetic field which is in every point proportional to the intensity of magnetization. And in spite of the discrepancies between Langevin's kinetic theory and experimental results, Weiss found that the relation between the absolute temperature and the saturation value of magnetization holds over a wide range of temperature in the case of magnetite, for smaller ranges only in Fe, Ni and Co. At lower temperatures there are very considerable discrepancies again between temperature and magnetization. But the most convincing proof of the existence of the molecular field of Weiss exists in the variation of the specific heat in the neighborhood of the critical temperature. There must be a good deal of truth in the intrinsic molecular field. I have in an article published in the Physical Review, March, 1910, page 359, tried to calculate the absolute magnetic moments of the elementary magnets of iron, nickel and magnetite. The equations applied were those given by Weiss' theory:

$$a = \frac{mNT}{rT}$$

$$\frac{T}{Tm} = \frac{a}{3}$$

which is true for the absolute temperature Θ, where the spontaneous magnetization disappears.

$$a = \frac{mNTm\ a}{3rT} \text{ or}$$

$$m = \frac{3r\Theta}{NTm}$$

This calculation of m, the moment of the elementary magnets presupposes that the theoretical temperature relation holds from the critical temperature down to the absolute zero.

The values taken and the results are contained in the next table.

TABLE 1

Substance	Tt=20	Tm	Θ	N	NT = Hm	m10^{20}	$\mu_H 10^{24}$
Fe	1860	2120	756	3,850	6,560,000	5.15	1.66
F_3O_4	430	490	5362	33,200	14,300,000	2.02	0.93
Ni	500	570	376	12,700	6,350,000	3.65	4.8
Co	1421	1435	1075	6,180	8,870,000	6.21	3.24
Heusler Alloy	.....	518	310	12,940	6,700,000	3.55	1.60

The values for cobalt are taken from a thesis of W. W. Stifler[1] the values for Heusler alloy from a thesis of P. W. Gumaer.[2] μ_H is the mass of a hydrogen atom. If we divide 4.8 by 3 we find for this fundamental quantity 1.6, if we divide the value of cobalt by 2 we find 1.62, the average value of μ_H being $1.5 \cdot 10^{-24}$; $\frac{e}{\mu_H} = 9654$ thus $e = 1.45 \cdot 10^{-20}$. This value agrees well with that due to Rutherford. Thus the magnetic properties give an indirect method of determining this fundamental quantity of nature. This fact seems to me also to go to support the theory of Weiss of the intrinsic magnetic field. One further assumption has been made in this calculation, which is very important:

$a = \frac{mNT}{rT}$, where r is determined in the kinetic theory of gases by the following equation:

$$rN_1T = p$$

N_1 is the number of molecules of a gas in unit volume under the pressure p and at the temperature T. rT is twice the kinetic energy of a molecule corresponding to one degree of freedom. By extending this equation to the magnetic molecules of ferromagnetic metals, we assume that these molecules have the same degrees of freedom of rotation as the molecules of a gas. If we do this we come to the conclusion that the magnetic molecule of iron consists of 2, that of nickel of 6, and that of cobalt of 4 atoms.

---

[1] W. W. Stifler, Phys. Rev. v. 33, p. 268, 1911.

[2] P. W. Gumaer, Phys. Rev. 1912.

V

THE MAGNETON OF P. WEISS

From recent magnetic investigation at very low temperature and at temperatures above the critical one, P. Weiss, in a number of articles published in the Comptes Rendus and in the Journal de Physique, has drawn another conclusion, which is confirmed by further investigations, means a fundamental progress in our knowledge of nature.

The molecular moments of magnetization were determined at the temperature of liquid hydrogen. P. Weiss gives the following values:

For iron,	12,360
For nickel,	3,370
For cobalt,	10,042
For magnetite,	7,417

If we divide the first number by 11, the second by 3, the third by 9 and the last by 6, we find 1123.5, thus iron cobalt and nickel have a common divisor, while magnetite seems to deviate considerably. P. Weiss calls this value the magneton-gram. Above the critical temperature the magnetite follows Curie's rule over certain intervals of temperature.

If σ_m represents the magnetic moment of the gram-molecule, its maximum value at absolute zero, then Langevin's theory of paramagnetic gases gives:

$$\frac{\sigma_m}{\sigma_{m\circ}} = \text{Aga} - \frac{1}{a}$$

where

$$a = \frac{\sigma_{m\circ} H}{rT}$$

By developing $\text{Aga} - \frac{1}{a}$ in a series and neglecting every term besides the first, we get:

$$\frac{\sigma_m}{\sigma_{mo}}=\frac{a}{3}=\frac{\sigma_{mo}H}{3rT};\ \chi_m=\frac{\sigma_m}{H}=\frac{\sigma_{mo}^2}{3rT}$$

and Curie's constant is equal to:

(1)
$$C_m=\chi_m T=\frac{\sigma_{mo}^2}{3r}$$

$r=83,155.10^6$ ergs per degree,
or, writing the equation for unit mass:

$$C=\frac{m\sigma_o^2}{3r}$$

If χ and $\frac{1}{T}$ are represented graphically, there appear four or five straight lines, giving five values for the constant C; this can be explained either by the assumption that *m* or *r* varies, or two or three quantities together. P. Weiss shows that the variation of *m* alone does not explain the observations, but that these constants may be correlated by the assumption that σ_o varies abruptly from one value to the other in very simple ratios. But it is surprising that with increasing temperature the magnetic moment per unit mass should increase in the ratio 1: 1.25: 1.5: 2: 2.5. In Langevin's original theory the magnetic moment is independent of the temperature; here it appears to increase in regular steps abruptly. But on the basis of the theory of Langevin which has as yet no direct experimental support, we may also assume that the degrees of freedom vary more or less abruptly so that Curie's constant increases with increasing temperature, or *r* decreases

$$rT=\frac{2L}{n}$$

where *n* is equal to the number of degrees of freedom. If *r* decreases with increasing temperature, we see that the number of degrees of freedom *n* increases, and this seems to me much more probable than the increase of the magnetic moment with rising temperature; the molecule of F_3O_4 is complicated enough to allow at higher temperature an increase of the degrees of freedom.

P. Weiss supplies afterwards equation (1) to dissolved paramagnetic substances. Still considering the underlying diamagnetism of Langevin, and assuming that the diamagnetic atoms in the compounds with paramagnetic substances conserve their diamagnetism, P Weiss corrects the value of Pascal and finds corrections amounting to from 1 to 6%.

TABLE 2

Substance	$X_m 10^6$	σ_{mo}	$n=\frac{\sigma_{mo}}{1123.5}$	n'	n''
K and NH_4 ferricyanide	1,730	11,700	10.41	10	1.04
Fe and NH_4 pyrophosphate	7,990	24,600	21.89	22	2.19
Fe and NH_4 citrate	8,040	24,680	21.96	22	2.19
Na – Ferripyrophosphate	9,660	27,100	24.04	24	2.40
Na – Ferrimetaphosphate	13,000	31,500	28.03	28	2.8
Ferrichloride	13,100	31,390	27.93	28	2.8
Ferrisulfate	15,200	33,800	30.09	30	3.0
K – Ferrometaphosphate	11,300	20,200	25.99	26	2.6
Na – Ferrooxalate	12,300	30,480	27.11	27	2.7
Na – Ferropyrophosphate	13,000	31,370	27.91	28	2.8
Ferrosulfate	12,900	31,120	27.69	28	2.8

If we displace the decimal point by one cipher to the left, we
have for *n*: a series of values which is a little more deviating
1.04 from integers than Weiss' value But it would be
2.19 interesting to see the values without that doubtful
2.19 correction. If this series were correct, the magneton
2.40 gram in these substances would be ten times larger
2.8 than in the ferromagnetic metals. If we displace
2.8 the decimal point in the other direction we find an-
3.0 other common divisor of σ_{mo}, which would make the
2.6 magneton ten times smaller than in the iron, nickel
2.7 and cobalt. After the introduction of that doubtful
2.8 correction, P. Weiss finds among 27 substances meas-
2.8 ured by Pascal only 17 for which the agreement is satisfactory. This is a little more than half of the salts chosen.

The theory of Langevin is furthermore extended to magnetic salts in the solid state. The results are given in the following

TABLE 3

Substance	$X_m 10^6$	σ_{mo}	$n = \frac{\sigma_{mo}}{1123,5}$	n″
$FeCl_3$	14,650	32,400	28.83	2.88
$FeCl_3 2NH_4ClH_2O$	12,830	30,330	26.99	2.69
$FeF_3 3NH_4F$	14,820	32,660	28.94	2.89
$FeF_3 2NH_4F\ H_2O$	14,965	32,800	29.19	2.92
$FeF_3 3H_2O$	7,899	32,860	21.23	2.12
Ferriacetylacetonate	10,922	28,150	25.05	2.50
Mn_3O_4	5,730	20,190	17.97	1.80
Cl_rCl_3	7,027	22,510	20.04	2.00
Cobaltacetylacetonate	7,767	23,730	12.12	2.11
$\frac{1}{2}$ $Cr(NH_3)_6Cr(Cr_2O_4)_2 3H_2O$	7,080	22,650	20.16	2.00
$\frac{1}{2}$ $Cr(NH_3)_4C_2O_4Cr(NH_3)_2(C_2O_4)_2 3H_2O$	7,080	22,650	20.16	2.00

Here it is much more interesting to displace the decimal point towards the left by one cipher. We find the following values:

2.88
2.69
2.89
2.92
2.12
2.50
1.80
2.00
2.11
2.01
2.01

a series which agrees, with one exception, even better with whole numbers than that of Weiss. By these common divisors the magneton gram would be ten times larger than in the strongly magnetic metals. Above the critical temperature the strongly magnetic metals seem to follow Curie's rule, and from these constants Weiss found again a common divisor, which is very satisfactory for nickel and cobalt, unsatisfactory for iron without the assumption of polymerisalions. Pure nickel at high temperatures has 8 magnetons; at the limit of the nickel iron alloys it has 9, at very low temperatures 3, and in the solutions 16 magnetons. R. H. Weber[1] has given the susceptibilities of the salts of the iron group. Among nine or eight values only three show a well-defined common divisor. If magnetism can be broken up into magnetons as an electrical charge can be divided in electrons, it should be possible to isolate the magneton, as it was possible to isolate the electron.

[1] Annalen der Physik, Vol. 36, p. 624, 1911.

Abstract

SOME PHYSICAL CONSTANTS OF SULPHUR TRIOXIDE. MELTING- AND BOILING-POINTS, DENSITY, COEFFICIENT OF EXPANSION AND MOLECULAR WEIGHT

By D. M. Lichty

University of Michigan, Ann Arbor, Mich.

Both the persistently liquid or α-sulphur trioxide and the ordinary solid or β-variety were investigated. The α-trioxide, prepared by carefully dehydrating ordinary oxide over phosphorus anhydride, melts at 16.79° (corr.) and boils at 44.88° under 760 mm. pressure. The melting- and boiling-points are generally given as 15° and 46°, respectively.

The density at intervals from 11.8° to 48° and the co-efficient of expansion between the same intervals are given in Table I.

Schultz-Sellak[1] found 0.0027 for the coefficient of expansion between 25° and 45°, and Schenck[2] 0.0023 between 11° and 35.3°.

The molecular weight of both the α and β-varieties, as calculated from the freezing-point depression of phosphorus oxychloride, is 80, as the data in Tables II and III show.

These results show that the α and β-varieties of sulphur trioxide behave essentially alike in phosphorus oxychloride, and have like molecular weights. The first column of molecular weights was calculated with K=69, a value used by Oddo[3], the second column with 76.8, published recently by Walden.[4]

Oddo found that the molecular weight of the α-trioxide is 80, but that of the β-trioxide was 160.

It has also been found that, contrary to Schenck's[5] observation, the α-trioxide does not attain constant volume with unusual slowness when warmed or cooled to 35°.

[1] *Ber.*, *3*, 215.

[2] *Ann.*, *316*, 1.

[3] *Gaz. Chim. 31. II*, 141, 163, 165.

[4] *Z. anorg. Chem.*, *68*, 307–16.

[5] *Loc. cit.*

TABLE I

Temp.	Density	Coeff. Expan.
11.8°	1.9457	
		0.000676
15	1.9422	
		0.002005
20	1.9229	
		0.002204
25	1.9020	
		0.002363
30	1.8798	
		0.002466
35	1.8569	
		0.002671
40	1.8324	
		0.002754[1]
45	——	
		0.002805
48	1.7921	
11.8°–35°	——	
		0.002066
25°–48°	——	
		0.002665

TABLE II

Variety	Conc.	Depr.	Molecular Weights.	
β	0.817	0.731	77.07	85.80
β	1.479	1.343	76.00	84.61
β	2.154	2.019	73.60	81.94
α	2.902	2.796	71.63	79.85
α	3.637	3.595	69.79	77.69

TABLE III

α	0.882	0.813	74.82	83.30
α	1.540	1.435	74.08	82.28
β	2.297	2.214	71.57	79.68
β	3.152	3.139	69.28	77.13

---

[1] By interpolation.

Abstract

THE CONSTITUTION OF ALUMINATES

By Edward G. Mahin
Purdue University, LaFayette, Indiana

Aluminium and aluminium hydroxide dissolve in strong bases and it is at present believed that salts of a hypothetical "aluminic acid" (aluminium hydroxide ionized as an acid) exist in the solutions thus formed. A consideration of the properties of aluminium indicate a doubt as to the correctness of this view. Investigations of others are shown to be not entirely in harmony with the theory. In this paper is given an account of experimental work to determine (1) the heat of solution of aluminium hydroxide in sodium hydroxide, (2) the quantity of aluminium hydroxide precipitated from a sodium aluminate solution by a known weight of ammonium nitrate and (3) the relative weights of aluminium oxide and oxygen produced by the electrolysis of sodium aluminate. From the results obtained the author concludes that the colloidal character of aluminium hydroxide is a more important factor in conditioning its solubility in bases than is its amphoteric character. It is even doubted whether the substance is amphoteric at all, as this term is generally understood.

REPORT BY CHARLES MARIE IN THE NAME OF THE PERMANENT COMMITTEE OF THE INTERNATIONAL COMMISSION ON THE PUBLICATION OF ANNUAL TABLES OF CONSTANTS AND NUMERICAL DATA OF CHEMISTRY, PHYSICS AND TECHNOLOGY, APPOINTED BY THE SEVENTH CONGRESS OF APPLIED CHEMISTRY (LONDON, 1909).

Gentlemen:

If we were to give you in this report a detailed statement of the work and actions of the International Commission since the Congress in London, it would take too long, and we therefore ask you to allow us to condense the report into a statement of the most important facts.

A first general assembly of the Commission met in Paris in October, 1909, and delegated the necessary powers to administer the business of the Commission to a standing (permanent) committee, consisting of representatives of Germany, England, Holland and France (one from each of these countries), the representative of France being given the title and duties of General Secretary. This standing committee, to which later a representative of Italy was added, consists at the present moment of Professors M. Bodenstein (Hanover), Bruni (Padua), Ernest Cohen (Utrecht), Dr. C. Marie (Paris), and Dr. N. T. M. Wilsmore (London).

This standing committee, which was formed with the special purpose of rendering *meetings* of the committee *convenient*, held two meetings in 1910 and two in 1911; its last meeting was held in March, 1912, after the publication of the first volume.

This first volume of Annual Tables, which we present to the Congress, will tell you, better than any person could, what the work of the International Commission has been; it is not for us to pass judgment on this work. We must, however, call your attention to the importance of the work: it will constitute for everybody a revelation of the amount of work being done in the laboratories of the world! This very fact is in itself a demonstration of the usefulness and need of the work that has been done. Thanks to the Annual Tables we feel sure that everything in the domain of physics and chemistry, pure and applied, which may be expressed in numbers, will be catalogued. The value of this systematic work of organization has, further, received a first consecration by the recognition of the International Association of Academies.

Such an undertaking could be conducted only at a great cost, and you will find appended to this report, advisedly kept brief, a statement of the financial position of the Commission, which acknowledges gratefully all the generous contributions that made it possible for the Commission to meet the heavy expenses it was obliged to incur. Governments, Academies Scientific and Industrial Societies, private individuals, solicited by members of the International Commission, have hitherto furnished the sums necessary for the undertaking.

Unfortunately, as the value and importance of the volume just published demonstrate the usefulness of this publication in a most striking manner, so also has the *estimated cost* of publication been far *surpassed.* Those among you who received the first subscription blanks in October (1911), will remember that we promised to our subscribers a volume of at least 300 pages; we have published a volume of 766 pages! Our expenses consequently were increased, and in the same proportion, whereas the price of the volume was not changed. We do not know, as yet, how the work done will be judged in the world of science and of industry; we only know that the principle of the Tables must have been considered important, since the call, alone, for subscriptions, was answered by more than 800 subscribers, and we have, on the basis of this number, decided on the printing of 2000 copies; we may expect that this will be barely sufficient.

However, under the most favorable circumstances and without counting the losses incidental to commerce, it is impossible to obtain a sufficient revenue to pay the annual expenses from the sale of the volume at the price it is offered. It would be necessary, in order to obtain such a return, to effect the sale of more than 3000 copies or to increase decidedly the price of the volume.

The latter course could not be followed, excepting on a small scale; it would entail the risk of shutting out, at once, a large number of would-be buyers, and would, at all events, be a dangerous experiment. The sale of larger numbers appears to us as more likely, but can only gradually be attained; it is therefore indispensable that the International Commission receive endowments and contributions in order to continue its work.

We trust that you will recognize the intense effort involved in the work already accomplished and that you will give us the necessary authority to obtain the indispensable financial support which the work demands.

For the International Commission, the Permanent Committee:

Professor Bodenstein,
Professor Bruni,
Professor Ernest Cohen,
Dr. N. T. M. Wilsmore,
Dr. Charles Marie,
General Secretary.

Paris, June 15, 1912.

TABLES ANNUELLES DE CONSTANTES ET DONNEES NUMERIQUES DE CHIMIE DE PHYSIQUE ET DE TECHNOLOGIE

COMITE INTERNATIONAL DE PUBLICATION

Etat général des Recettes et Dépenses arrêté au 10 mai 1912

Recettes (Détail p. 2-6)

	Francs	
1909-1910	22.761,46	
1911	20.276,54	
1912	13.353,10	
Intérêts du Compte de dépôt	60,95	
		56.452,05

Depenses (Résumé ci-dessous)

	Francs	
1909-1910	20.306,50	
1911	15.561,05	
1912	14.368,25	
	50.235,80	
En caisse au Crédit Lyonnais	6.070,55	
En caisse au Secrétariat	145,70	
		56.452,05

Le Secrétaire général Trésorier:
C. Marie.

SUBVENTIONS

Résumé des Recettes (Détail p. 2 et suiv.)

	1910 Francs	*1911* Francs	*1912* Francs
Allemagne	614,25	4.163,00	3.808,80
Autriche	6.915,36	1.651,95	1.669,95
Belgique	27,00	1.651,95	100,00
Danemark	27,00	100,00	100,00
Empire Britannique	2.468,75	2.011,20	100,00
Espagne	2.468,75	400,00	100,00
Etats-Unis	1.549,00	776,40	100,00
France	5.750,00	6.800,00	4.499,90
Hollande	1.462,90	1.674,40	4.499,90
Hongrie	1.462,90	1.674,40	2.090,00
Japon	150,00	150,00	150,00
Norvège	150,00	557,49	150,00
République Argentine	150,00	557,49	200,00
Roumanie	150,00	300,00	200,00
Russie	2.674,50	300,00	200,00
Suède	626,20	142,10	43,20
Suisse	626,20	1.550,00	43,20
	22.237,96	20.276,54	12.861,85

Ensemble: 55.376,35

Report	55.376,35
Souscriptions perpétuelles (1910) Dr. L. Haitinger (Weidling) et (1912) Prof. v. Goldschmidt (Heidelberg) ensemble	1.014,75
Intérêts du compte de dépôt	60,95
Total des recettes au 10 mai 1912	56.452,05

Résumé des Dépenses (Détail p. 7 et suiv.)

	1909-1910	*1911*	*1912*	*Totaux*
Secrétariats nationaux (Détail p. 7)	9.821,20	13.173,05	3.703,25	26.697,50
Collaborateurs extracteurs (Détail p. 9)	10.485,30	2.388,00 (1er semestre)	....	12.873,30
Tabulateurs (Vol. I)	....	....	10.665,00	10.665,00
	20.306,50	15.361,05	14.368,25	50.235,80

DETAIL DES SUBVENTIONS

Reçues par le Comité international depuis le début jusqu'au 10 mai 1912

Les subventions sont placées dans la colonne de l'année où elles ont été *versées* au Compte du Comité.

Pays	*Nom des Donateurs*	*1910* Francs	*1911* Francs	*1912* Francs
Allemagne.	Deutsche Bunsen Gesellschaft	614,25		
	Industrieller Verein Mulhausen		100,00	
	Königliche Akademie der Wissenschaften zu Berlin		1.232,00	

Pays	*Nom des Donateurs*	*1910* Francs	*1911* Francs	*1912* Francs
Allemange.	Schimmel u. C° Miltitz bei Leipzig........		616,00	615,00
	Chemische Fabrik, Griesheim-Elektron, Frankfurt a. Main..........		616,00	615,00
	Königliche Sächsische Gesellschaft der Wissenschaften-Leipzig...			368,40
	Verein deutscher Eisenhüttenleute..........		123,00	122,80
	Siemens u. Halske, Siemens-Schuckert-Werke (Berlin)......		615,00	614,00
	Allgemeine Elektrizitäts-Gesellschaft (Berlin)..		615,00	614,00
	Bergmann Elektrizitäts-Werke (Berlin).......		246,00	245,60
	Verein deutscher Ingenieure................			614,00
		614,25	4.163,00	3.808,80[1]
Autriche.	Verein österreichischer-Chemiker.........	104,70		104,35
	Kaiserliche Akademie der Wissenschaften in Wien..............	6.287,66		
	Osterreichischer Ingenieur u. Architektenverein (Wien)......		73,20	
	Gouvernement Autrichien		1.578,75	1.565,60
	Chemische physikalische Gesellschaft (Wien).	523,00		
		6.915,36	1.651,95	1.669,95
Belgique.	Mr. W. Spring (abandon d'honoraires)	27,00		
	Société chimique de Belgique............			100,00
		27,00		100,00
Danemark.	Société chimique de Danemark........		100	100
			100	100
Empire Britannique.	J. Brown, Esq., F.R.S. (Belfast)..........	79,25		
	The Rt. Hon. the Earl of Berqueley, F.R.S...	1.258,00		
	Royal Dublin Society...	250,00	252,50	
	Royal Irish Academy...	125,50		

[1] *Allemagne.* — Deutsche chemische Gesellschaft.— Par suite d'un retard dans la transmission la subvention de cette société en 1912 (500 Marks) ne figure pas sur cette liste.

Pays	*Nom des Donateurs*	*1910* Francs	*1911* Francs	*1912* Francs
Empire Brittanique.	British Association for the Advancement of Science...........	756,00	753,60	
	Chemical Society.......		252,40	
	Royal Society of Edinburgh.............		126,15	
	Society of Chemical Industry............		251,50	
	Faraday Society........		126,20	
	Royal Society of Canada		248,85	
		2.468,75	2.011,20	
Espagne.	Académie royale des Sciences (Madrid)..		250,00	
	Société espagnole de Physique et de Chimie		150,00	
			400,00	
Etats-Unis.	American Academy of Arts and Sciences...	1.290,00		
	American Electrochemical Society...........	259,00		
	American Chemical Society...........		776,40	
		1.549,00	776,40	
France.	Association des anciens élèves de l'Ecole de Physique et de Chimie	100,00	100,00	
	Société chimique de France............	500,00	500,00	500,00
	Association française pour l'avancement des Sciences...........	500,00	500,00	
	Société Industrielle de l'Est..............	100,00	100,00	
	Société d'Encouragement pour l'Industrie nationale............	1.000,00	1.000,00	
	Association des Chimistes de Sucrerie et de Distillerie..........	50,00		
	Société française de Physique.........	500,00	500,00	
	Gouvernement français..	3.000,00	3.000,00	2.999,90
	Société de Chimie-physique (Paris)....		100,00	
	Académie des Sciences...		1.000,00	1.000,00
		5.750,00	6.800,00	4.499,90

Pays	*Nom des Donateurs*	*1910* Francs	*1911* Francs	*1912* Francs
Hollande.	Congrès néerlandais pour les Sciences exactes et médicales.	522,45	523,25	
	Institut royal des Ingénieurs à la Haye (Section d'Electrotechnique).	209,00	209,30	
	Société d'Utrecht pour les Sciences et les Arts.	522,45	523,25	
	Société pour l'avancement des Sciences (Amsterdam).	209,00	209,30	
	Société chimique néerlandaise.		209,30	
		1.462,90	1.674,40	
Hongrie.	Gouvernement.			2.090,00
				2.090,00
Japon.	Chemical Society (Tokyo)	100,00	100,00	100,00
	Scientific Agricultural Society.	50,00	50,00	50,00
		150,00	150,00	150,00
Norvège.	Nansenfond (Christiania)		557,49	
			557,49	
République Argentine.	Sociedad cientifica Argentina.			200,00
				200,00
Roumanie.	Laboratoire d'acoustique et d'Optique (Bucarest).		300,00	200,00
			300,00	200,00
Russie.	Gouvernement russe. . . .	2.674,50		
		2.674,50		
Suède.	"Jernkontoret" (Stockholm).	274,65		
	Studentengesellschaft (Upsala).	351,55		
	Souscriptions diverses receuillies par M. le Docteur L. Ramberg (Lund).		142,10	
	Kemistsamfundet (Stockholm).			43,20
		626,20	142,10	43,20

Pays	*Nom des Donateurs*	*1910* Francs	*1911* Francs	*1912* Francs
Suisse.	Société de Physique et d'Histoire naturelle de Genève.........		100,00	
	Société Suisse de Physique		100,00	
	Sté de Chimie du Haut-Rhin.............		50,00	
	Gouvernement Suisse...		1.000,00	
	Société Suisse de Chimie.		100,00	
	Société de Chimie de Genève...........		100,00	
	Société Vaudoise des Sciences naturelles..		100,00	
			1.550,00	

DETAIL DES DEPENSES DU COMITE INTERNATIONAL

Depuis sa création (juin 1909 jusqu'au 10 mai 1912)

1°—Dépenses des Secrétariats nationaux

	1909–1910 Francs	*1911* Francs	*1912* Francs
Allemagne........................	1.181,45	1.019,30 au 10 mai 1911[1]	
Autriche.........................	71,40	365,15	
Danemark........................	......	217,75	
Empire Britannique...............	1.693,55	984,55	
Espagne.........................	400,00	......	
Etats-Unis.......................	131,95	188,00	
France (Secrétariat Général) (Détail feuille 8).....................	5.475,70	9.493,25	3.703,25
Hollande.........................	497,40	238,00	
Italie...........................	139,45	341,10	
Japon...........................	4,65	4,85	
Norvège.........................	......	50,55	
Russie..........................	......	75,10	
Suède...........................	18,90	195,45	
Suisse..........................	206,75		
	9.821,20	13.173,05	3.703,25

---

[1] Les dépenses des Secrétariats nationaux pour le 1er semestre 1912 ne seront connues que plus tard.

DETAIL DES DÉPENSES DU SECRETARIAT DE PARIS

	1909–1910 Francs	*1911* Francs	*1912* Francs 1 janvier à 10 mai
Frais de bureau	631,15	193,35	42,85
Impressions	826,65	3.663,65	643,20
Secrétaires adjoints	2.800,00	3.700,00	1.666,00
Collaborateurs temporaires[1]	115,50	783,25	717,00
Frais de poste	535,05	819,45	229,50
Dépenses diverses	567,35	233,55	404,70
	5.475,70	9.493,25	3.703,25

FRAIS D'EXTRACTION DES PERIODIQUES

	1910 *1er et 2e semestres* Francs	*1911* *1er semestre* Francs	*1912* *2e semestre* Francs
Allemagne	4.146,00	577,00	126,00[2]
Autriche	558,00	97,00	
Belgique	27,00	......	
Danemark	....	32,00	
Etats-Unis	721,00	338,00	
Empire Britannique	2.100,00	776,00	
France	808,30	......	
Hollande	727,00	......	
Hongrie	....	79,00	
Italie	672,00	135,00	
Japon	48,00	......	
Russie	372,00	134,00	
Suède	179,00[3]	94,00	
Suisse	127,00	......	
	10.485,30	2.262,00	126,00

---

[1] On comprend sous ce titre les honoraires attribués pour des travaux spéciaux (Traductions-Organisation de la souscription au premier volume, etc.).

[2] Cette somme représente un versement anticipé fait à deux collaborateurs — L'ensemble de ces dépenses d'extraction du 2e semestre 1911 sera règlé avant le 30 juin; il s'élève à la somme de 6300 francs environ.

[3] Cette somme représente l'extraction dans les pays scandinaves qui, depuis 1911, sont représentés au Comité international par des délégués différents.

THE VAPOR PRESSURES OF SOME CONCENTRATED ZINC CHLORIDE SOLUTIONS

BY ALAN W. C. MENZIES AND HENRIK BOVING
Oberlin College, Oberlin, Ohio

The measurements of vapor pressure here described became necessary, for the purposes of another investigation, when it was found that the data required were absent from the existing literature.

Qualitative analysis of the zinc chloride[1] employed showed the essential absence of impurities other than traces of sulphate and of arsenic. Quantitative analysis of a very concentrated solution for zinc and for chlorine indicated the quantity of basic salt present as 1.23% reckoned as Zn (OH) Cl. After addition of the calculated quantity of hydrochloric acid required to convert this to normal salt, solutions containing 60, 65 and 70 parts of $ZnCl^2$ per 100 parts of solution were prepared by suitable dilution.

The vapor pressures were measured by means of tensimeters of the Bremer-Frowein type, with oil as manometer fluid and phosphorus pentoxide as drying agent. In order satisfactorily to evacuate the tensimeter without the danger of concentrating the zinc chloride solution under investigation, the bulb containing the latter was immersed in a mixture of alcohol and solid carbon dioxide contained in a Dewar vessel. By means of a mercury pump it was then easy to reduce the pressure, before sealing off, to a few hundredths of a millimeter, as registered by a MacLeod gauge.

In measuring rather low vapor pressures by this method, the chief source of error lies in the presence of permanent gases that escape slowly from the substances in the tensimeter. For this reason, the oil and the zinc chloride solution were freed as far as possible from air beforehand. As it is not possible, however, entirely to avoid dissolved gases, since these may enter during the process of charging the tensimeter, it is necessary to have recourse to a process of equalizing the gas pressure on opposite sides. If the volume of the bulbs is very large in comparison with that of the manometer tube, and if the pressure of permanent gas is but small, this may be effected satisfactorily by placing the tensimeter in a horizontal position, thus putting the opposite sides in communication, and again erecting. In order that the permanent gas should distribute itself uniformly throughout the apparatus when in the horizontal position, it was found essential that all appreciable water vapor be removed from the apparatus by placing the bulb containing the solution, which was suitably bent back for this purpose, in a mixture of alcohol and solid carbon dioxide for two and a half hours. Otherwise the permanent gas on the side of the solution was invariably more humid than that on the side of the phosphorus pentoxide, and the distribution of permanent gas consequently unequal. To insure that the actual pressure of permanent gas was small, each tensimeter was re-exhausted after having been set up for several days. Absence of an uneven distribution of permanent gas was confirmed by the readings remaining identical after many days, during which the temperature had been varied in both directions; and also by constancy of reading after the tensimeters had again been placed in the horizontal position.

---

[1] This was the "chemically pure" product of Baker and Adamson.

The tensimeters were immersed in a glass-sided water tank thermostat, constant by automatic regulation to two hundredths of a degree, and reached equilibrium within one hour. The temperature measurement, made by thermometers standardized by means of the transition point of Glauber's salt to anhydrous sodium sulphate and also by indirect comparison with the Sèvres standards, is believed accurate to a few hundredths; while the pressure measurement is believed accurate to 0.1 mm. of mercury.

VAPOR PRESSURE OF ZINC CHLORIDE SOLUTIONS

Parts per 100 parts solution	**Pressure in mm. mercury at 0°,**		
	14.64°	24.64°	29.60°
60	4.4	8.1	10.8
65	2.5	5.0	6.9
70	1.4	2.9	4.1

CONTRIBUTIONS A L'ETUDE DES SAVONS

PAR PROF. DR. A. REYCHLER
St. Nicholas (Waas) Belgium

I. La cristallisation des palmitates acides de sodium

Les recherches que j'ai faites sur le sujet indiqué par ce premier sous-titre ont été décrites dans le fascicule jubilaire de la Société Chimique de Belgique (mai 1912), de sorte qu'il suffira d'er rappeler ici les conclusions.

Les solutions étendues de palmitate de sodium commencent à cristalliser à une température qui, d'accord avec les indications de Krafft,[1] est comprise entre 47° et 37°, et qui cet d'autant plus élevée que la concentration saponine est plus forte. Le processus a ceci de particulier qu'il s'avive d'une manière très prononcée à quelques degrés au dessous de l'apparition des premiers cristaux, et qu'il s'achève presque intégralement en un petit intervalle de température.

Lorsque la normalité des solutions est assez élevée (de 0,05 à 0,02), les premiers cristaux sont nettement reconnaissables au sein d'une liqueur transparente, et la cristallisation pent être qualifiée de *nette en milieu limpide.*—Lorsque la normalité est inférieure à 0,02 les solutions sont plus ou moins troubles à haute température, et manifestent un châtoiement caractéristique un peu en deçà de 50°. Leur cristallisation se prononce vers 43° à 37°, et produit un enchevêtrement de cristaux trés fins: elle est *confuse en milieu trouble.*—Les solutions les plus étendues (de normalité 0,0025 par exemple) donnent des agglomérats presque grenus, très aptes à former dépôt.

Nos constatations résultent non seulement de l'observation directe des phénomènes, mais aussi de l'étude de la conductivité électrique des systèmes considérés. Cette conductivité diminue à température descendante, et signale par une chute rapide la période de cristallisation relativement active.

---

[1] D'après Krafft, *Ber. d. D. chem. Ges. 28*, 2571, la température de cristallisation serait toujours voisine de 45°.

Il est à remarquer enfin que tous les systèmes étudiés ont accusé aux basses températures (de 30° à 18°) des conductivités tellement voisines, que les courbes représentatives en arrivaient à se confondre.

Les eaux-mères des différentes cristallisations étaient donc probablement de composition très semblable.

II. Les eaux-mères des palmitates acides

Dans une série de publications très intéressantes, Krafft et ses collaborateurs ont mis en lumière la relation qui existe entre la composition de certains savons acides et la concentration des milieux qui leur ont donné naissance.

[1]Au sujet du palmitate de sodium il nous apprend qu'une solution d'un gramme de savon neutre dans telle quantité d'eau dépose du savon acide renfermant tel pour-cent de sodium; et il assure en même temps que l'eau-mère de la cristallisation ne retient qu'une trace absolument négligeable d'acide gras. Mais il ne nous dit rien quant au degré d'alcalinité de l'eau-mére, ni quant au rendement en savon acide. L'omission paraît regrettable et demande réparation.

Lorsqu'une *mole* (278 gr.) de palmitate sodique donne la quantité équivalente d'acide libre, les diminutions corrélatives de la teneur en sodium et du poids de la matière organique sont de 8,27% et de 22 grammes. Lorsque toutefois la transformation n'est que partielle et s'arrête à la production d'un sel acide renfermant encore $S\%$ de sodium, les diminutions sont de $8{,}27-S\%$ et de 22 $\frac{8{,}27-S}{8{,}27}$ grammes.—L'acidification partielle *d'un gramme* de palmitate fournirait donc $1-\frac{22(8{,}27-S)}{8{,}27\times 278}$, c'est à dire 1—0,00957 (8,27—S) gr. de savon acide.—Or, la quantité de sel neutre contenue dans ce produit est proportionnelle à S. Elle se chiffre par $[1-0{,}00957\ (8{,}27-S)]\frac{S}{8{,}27}$ grammes et représente [1—0,00957(8,27—

---

[1] F. Krafft et A. Stern, *Ber. 27*, 1747; Krafft et H. Wiglow, *Ber 28*, 2566.— Autres mémoires de la même série: *Ber. 27*, 1755; *28*, 2573; *29*, 1328 et 1334; *32*, 1584 et 1596.

S)] $\frac{1000S}{8{,}27\times 278}$ *millimoles.* Et comme notre matière première, un gramme de savon neutre, valait approximativement 3,60 millimoles, il faut que 3,60—0,435 S [1—0,00957(8,27—S)] millimoles de savon se soient dédoublées en acide libre, combiné à la masse cristalline, et en base libre, demeurée dans la liqueur-mère.

L'application de ce calcul aux données expérimentales de Krafft conduit aux déductions qui se trouvent groupées dans notre *tableau I.* Or la dernière colonne de ce tableau nous apprend une chose très importante: elle nous dit, en effet, que *la concentration de la soude dans les liqueurs-mères* commence par décroître en même temps que la concentration globale des systèmes considérés, mais *tend à devenir constante dès qu'elle est descendue à une valeur voisine de 0,002 millimole par centimètre cube.*[1]

TABLEAU I. (*Un gramme de palmitate de sodium*)

Eau dissolvante	Savon acide				Liqueur-mère	
	S	Poids calculé	Teneur en:		Soude	Concentration de la soude
			Soude	Acide		
Gr.	%	Gr.	Millimoles		Mmoles	Mmoles par cm.³
200	7.01	0,988	3,01	3,60	0,59	0,00295
300	6,84	0,986	2,93	3,60	0,67	0,00223
400	6,60	0,984	2,82	3,60	0,78	0,00195
450	6,32	0,981	2,70	3,60	0.90	0,00200
500	6.04	0,979	2,60	3,60	1,00	0,00200
900	4.20	0,961	1,77	3,60	1,83	0,00203

La similitude de composition des eaux-mères fournies par des solutions diluées de palmitate de sodium se trouve donc annoncée par deux moyens d'investigation (titres I et II de ce mémoire). Pour confirmer le résultat de notre enquête nous avons estimé qu'il était nécessaire de *compléter l'étude analytique de nos systèmes diaphasés.*

---

[1] Les indications de Krafft concernant quelques cristallisations de stéarate, d'élaidate et d'oléate de sodium se prêtent á des déductions semblables aux précédentes, et démontrent également que la concentration de la soude dans les liqueurs-mères ne varie qu'entre des limites assez étroites (de 0,0028 à 0,0015 millimole par centimètre cube).

A cet éffet nous nous sommes servi de deux palmitates approximativement neutres, préparés à partir de sodium, d'alcool et d'acide palmitique pur (fusible à 62°,5). Le premier, que nous désignons par la lettre *A*, était faiblement acide et valait *par gramme* 3,543 millimoles de soude. Le second, que nous appelons *B*, représentait par gramme 3,592 mmoles de soude et 3,557 mmoles d'acide palmitique.

Tous les récipients employés étaient en verre d'Iéna ou en platine; et l'eau prise comme dissolvant était fraîchement distillée, et privée de CO_2 par quelques minutes d'ébullition. Quant au *mode opératoire*, il peut être brièvement indiqué de la manière suivante.

Une solution chaude l'environ 2 *gr. de palmitate* dans la quantité voulue d'eau est mise à cristalliser pendant trois jours, en fiole couverte[1]. Elle est ensuite filtrée à la pompe sur un disque de papier.

Le filtrat est pesé, afin que les données de son analyse puissent être rapportées à la totalité de la liqueur-mère. On le concentre éventuellement, et, après avoir ajouté à chaud une ou deux gouttelettes d'acide sulfurique, on laisse au *précipité d'acide gras* le temps de bien se former. Une simple filtration permet alors de séparer cet acide (destiné à être séché, repris par l'éther, isolé, pesé) d'avec un nouveau filtrat, dans lequel on dose *le sodium* à l'état de sulfate.

Le savon acide, séché sur assiette poreuse et dans le vide est pesé avec une approximation de ± 2 milligr. Pour l'analyser on en dissout une certaine quantité dans de l'eau chaude et on ajoute une dose non excessive d'acide sulfurique. L'ensemble est ensuite soumis à une série de changements de température, jusqu'à ce que *l'acide gras*, alternativement solide et fondu, finisse par surnager à l'état de fluide homogène. L'isolement et la pesée de cet acide n'offre aucune difficulté, non plus que le dosage du *sodium* dans la liqueur aquéuse.

Notre *tableau II* rend compte de deux séries d'expériences, dont les premières furent faites avec *le savon A*, les autres avec *le savon B*. La température finale des cristallisations fut de 18°,5 pour la *série A* et de 17° pour la *série B.* Toutes les données du tableau sont rapportées à l'emploi d'un gramme de palmitate. Les valeurs en soude et en acide sont exprimées en millimoles, et les concentrations en millimoles pour centimètre cube.

---

[1] On psé successivement: savon, fiole + savon, et (après cristallisation faite) fiole + savon + eau.

TABLEAU II. (*Un gramme de palmitate de sodium*)

		Savon acide				Liqueur-mère			
	Gr. d'*eau* par gr. de savon.	Poids	Na	Valeur en:		Valeur en:		Concentration:	
				NaOH	Acide	NaOH.	Acide	NaOH	Acide.
		(Gr.)	%	(Millimoles)		(Millimoles)		(Mmoles par cm)^3	
Série A.				Trouvée		Calculée	Tr.		
1	46,87	0,976	7,785	3,3034		0,240	0,0159	0,0051	0,00034
2	95,09	0,963	7,673	3,2135		0,3295	0,0286	0,0035	0,00030
3	389,10	0,956	6,966	2,8970		0,646	0,153	0,0017	0,00039
Série B				Tr.	Tr.	Tr.	Tr.		
1	74,23	0,984	7,584	3,245	3,513	0,312	0,019	0,0042	0,00026
1 bis	77,07	0,985	7,57	3,242	3,522	0,342	0,019	0,0044	0,00025
2	122,06	0,977	7,63	3,242	3,486	0,339	0,035	0,0028	0,00029
3	243,8	0,966	7,49	3,146	3,445	0,442	0,088	0,0018	0,00036
4	435	0,936	6,85	2,788	3,377	0,785	0,1543	0,0018	0,00035
5	588,3	0,913	6,45	2,560	3,321	1,0225	0,2004	0,00174	0,00034
6	814,67	0,893	5,66	2,197	3,281	1,4167	0,2463	0,00174	0,00031

Pour la *série A* la quantité de soude contenue dans les eaux-mères est calculée en tenant compte du poids et de la composition des savons acides. Pour la *série* B l'analyse complète du palmitate employé permet de faire le bilan des opérations analytiques, et de constater que la soude se retrouve presque intégralement, tandis que les dosages d'acide laissent un certain deficit (atteignant en moyenne 0,027 mmole pour l'ensemble d'un essai).

Les deux dernières colonnes du tableau II se rapportent à la composition des eaux-mères. Elles nous apprennent: 1° que la concentration de l'acide gras n'est pas négligeable mais prend une normalité voisine de 0,00035; et 2° que la concentration de la soude commence par être un peu forte (Série *B*, chiffres 0,0042 at 0,0028) mais accuse bientôt une tendance à devenir constante (chiffres 0,0018 et 0,00174). L'assurance donnée par Krafft concernant *l'absence* de l'acide gras dans les eaux-mères était donc pour le moins exagérée, mais *la grande similitude des phases liquides se vérifie parfaitement.*

Au point de vue de la mécanique chimique, il ne sera peut-être pas inutile de présenter la remarque suivante. Les solutions qui ont donné naissance aux systèmes *A3* et *B3, 4, 5 et 6* étaient toutes de normalité inférieure à 0,02, et doivent avoir cristallisé dans des conditions très semblables (d'une manière confuse, en milieu trouble et à partir d'une température assez basse). Or ce sont précisément ces mêmes solutions qui ont produit des eaux-mères de composition quasi constante. La coïncidence est de nature à faire supposer que les palmitates acides se sont formés par superposition de couches, le long d'un intervalle de température, et que ceux d'entre eux qui font équilibre à des eaux-mères à peu prés indentiques se trouvent probablement enrobés par des couches superficielles de composition peu variable.

III. L'extractibilité des solutions de palmitate et d'oléate de sodium par le toluol

Lors de la cristallisation d'une solution de palmitate l'acide ne peut se retirer du milieu aqueux qu'en entraînant une grande partie de la base présente. Mais les choses ne se présentent plus de la même manière lorsqu'on opère l'extraction de l'acide gras par quelque liquide semblable au toluol. La base alors ne prend aucune part à l'exode, mais reste dans la phase aqueuse tout en y devenante de plus en plus libre. Dans ses expériences de ce genre Krafft s'est complu à faire l'extraction quasi totale de l'acide palmitique par une série de traitements au toluol[1]. Nous avons touvé plus intéressant de mesurer l'effet produit par un traitement unique dans des conditions déterminées.

1. Essais d'orientation

A. Une solution d'un gramme *de palmitate de sodium* dans 700 gr. d'eau fut traitée, en fiole ouverte, par 200 centimètres cubes de toluol.

1° *A chaud* (vers 80°), en mélangeant les liquides par un mouvement giratoire.— Il s'est produit une émulsion très mousseuse, dont après refroidissement on a pu séparer 100 cm^3 de solution toluique. L'analyse de cette dernière a montré que l'extraction avait porté sur 0,624 gr. d'acide (68% de la quantité présente).

2° *A froid*, après cristallisation, en agitant le mélange.—Il y a eu production d'une suspension grossière, *non mousseuse*, et extraction de 0,07 gr. d'acide, c'est à dire de tout l'acide non engagé dans le savon cristallin.[2]

---

[1] *Ber. d. D. chem. Ges. 27*, 1752; *28*, 2566.

[2] 0,00035 x 0,256 x 700 = près de 0,07.

B. Une solution *d'oléate de sodium* (1 gr. dans 700 cm^3 d'eau) a été traitée par 200 cm^3 de toluol.

1° *A chaud*, en agitant le mélange.—Emulsion mousseuse très stable. Après deux jours d'attente on a pu isoler 25 cm^3 de solution toluique. Extraction de 0,67 gr. d'acide (environ 70% de la quantité présente).

2° *A chaud*, en remuant prudemment les liquides avec une tige de verre.—Emulsion moins fine et mousse moins abondante. Extraction de 0,502 gr. d'acide.

3° *A froid*, en agitant la masse.—Emulsion très mousseuse, intraitable même après trois jours d'attente.

4° *A froid*, en remuant doucement avec une tige de verre.—Extraction de 0,207 gr. l'acide oléique.

L'efficacité du traitement dépend donc en grande partie du mode opératoire; mais d'une manière générale on peut cependant tirer les conclusions suivantes. Pour être *mousseuse* et abondamment *extractible* la solution de palmitate doit être prise à une température supérieure à sa période de cristallisation. La solution d'oléate est indubitablement dans le même cas; mais comme elle ne cristallise pas bien vite, elle reste mousseuse et extractible à basse température. Les deux propriétés marchent parfaitement d'accord, et semblant dépendre des mêmes conditions premières, notamment de la mobilité de l'acide gras et de la solubilité de cet acide dans le liquide extracteur.—*La mobilité* que nous avons en vue ne demande point que la solution de savon renferme une forte proportion d'acide hydrolytiquement libre, ou même des gouttelettes d'acide simplement émulsionné. Vu l'énormité du coefficient de partage[1] la moindre trace d'acide libre est presque intégralement enlevable, et comme le mécanisme de l'équilibre hydrolytique peut constamment régénérer cette trace, il n'est pas étonnant que l'extraction puisse atteindre un haut degré d'efficacité. Une circonstance doit cependant finir par mettre un terme au processus: c'est l'accumulation de plus en plus grande de soude libre dans la phase aqueuse.—Quant à *la solubilité dans le toluol*, elle est assez différente pour les deux acides dont nous avons utilisé les sels sodiques. Pour l'acide oléique elle est déjà illimitée à la température ordinaire, tandis que pour l'acide palmitique elle est petite à basse température et ne devient illimitée qu'au voisinage du point de fusion.

---

[1] L'acide gras libre est presque absolument insoluble dans l'eau.

2. Essais quantitatifs

Ceux-ci n'ont été faits qu'à froid (16°), et sur des solutions d'oléate de sodium. Le savon mis en expérience valait 7,41% de sodium et 92,90% d'acide oléique. Il représentait donc par gramme 3,2217 mmoles de soude et 3,2943 mmoles d'acide. Des solutions de cet oléate furent soumises à l'extraction toluique, et, pour que les traitements produisissent leur effet maximum tout en ne donnant que très peu de mousse. ils furent institués de la manière suivante.

On introduisait chaque couple de phases dans un assez long tube, et après avoir bouché ce tube on le disposait horizontalement. Tous les jours, pendant une semaine entière, on relevait plusieurs fois tantôt l'un tantôt l'autre bout du tube, de manière à déterminer un transport ondulatoire des phases superposées et un renouvellement des surfaces de contact. Le huitième jour on redressait le tube, et on en expulsait la très grande partie de la liqueur toluique en se servant d'un dispositif semblable à celui qui surmonte une pissette. Pour connaître la quantité de l'acide extrait, il suffisait ensuite de distiller une partie aliquote de la solution toluique, et de peser le résidu acide dans le ballon distillatoire même[1].

Notre *tableau III* rend compte des résultats ainsi obtenus. Il rapporte toutes choses à l'emploi de 50 cm³ de phase aqueuse (bien que nos essais 4a et 4c aient porté sur des solutions saponines deux fois plus volumineuses).

Tableau III. (*Oléate de sodium a 7,41% de metal*)

	APRES EXTRACTION FAITE				Acide total (Mmoles)	% de l'extraction	Concentration de l'extrait (Mmoles par 50 cm³)
	Phase aqueuse		Phase toluique				
	50 cm³ valant NaOH (Millimoles)	Acide	Volume (cm³)	Acide extrait (Mmoles)			
1	3,335	3,262	50	0,148	3,410	4,3	0,148
2	1,667	1,566	50	0,139	1,705	8,1	0,139
3	0,834	0,713	50	0,139	0,852	16,3	0,139
3a	0,834	0,717	50	0,136	0,852	16	0,136
3b	0,834	0,732	30	0,121	0,852	14,2	0,202
4	0,417	0,286	50	0,141	0,426	33	0,141
4a	0,417	0,290	40	0,136	0,426	31,9	0,170
4b	0,417	0,306	30	0,121	0,426	28,4	0,202
4c	0,417	0,308	25	0,119	0,426	28	0,238

---

[1] Toute pesée était précédée de la dessication de l'acide oléique dans le vide.—En aucun cas il n'a été nécessaire de filtrer la solution toluique.

Pour les essais *1*, *2*, *3*, *3a* et *4*, mettant en oeuvre des volumes égaux des deux phases, la quantité de l'acide extrait reste constamment voisine de 0,14 mmole; et pour les autres expériences, où la dose de toluol se trouve réduite à 40, 30 et même 25 cm^3, le poids de l'extrait représente au minimum 0,12 mmole. L'acide gras est manifestement d'autant moins extractible que la phase aqueuse est plus riche en soude: *le pour-cent de l'extraction se montre inversement proportionnel à la concentration totale de la soude dans la solution saponine.*

L'interprétation plus approfondie des faits, au point de vue des lois de la mécanique chimique, rencontre de grandes difficultés. Si nous nous adressons aux essais les plus simples, et si nous admettons, par hypothèse, que la concentration de l'acide libre dans la phase aqueuse soit une fraction constante de 0,14, l'équilibre hydrolytique.

(Bioléate) Const. = (Base libre) (Acide libre)^2 demanderait qu'il y eût un rapport constant entre la concentration du bioléate et celle de la base libre. Or ce desideratum se vérifie approximativement pour les essais *1*, *2*, *3* et *3a*, mais pas du tout pour le N^o 4.

	(Bioléate)	(Base libre)	Remarques
1	1,631	1,704	L'unité de volume est 50 cm^3. On met: (Bioléate) = *Acide non exrait* et: (Base libre) = Base total^2— bioléate. La concentration de l'acide libre est supposée constante et très petite.
2	0,783	0,884	
3	0,357	0,477	
3a	0,358	0,476	
4	0,143	0,274	

Il est donc probable que l'équation ci-dessus n'est pas seule à régler les phénomènes, et que déjà pour nos essais *3* et *4* la prépondérance de plus en plus prononcée de la base libre attribue un rôle de plus en plus important à l'équation.

(Oléate neutre) Const. = (Base libre) (Acide libre). Prise isolément cette dernière se montre absolument inapplicable.[1]

---

[1] Rien ne nous dit d'ailleurs que l'association moléculaire doive s'arrêter à la formation du bisléate, ni que la présence du toluol assure l'homogénéité réelle de la phase aqueuse.

Appendice

Il ne sera pas inutile d'intercaler ici quelques renseignements concernant la conductivité électrique des solutions aqueuses d'oléate de sodium.

Tableau IV. (*Oleate à 7,41% de sodium*)
Conductivités électriques, à la température de 18°.

Dilution (Litres)	Normalité alcaline.	Conductivité spécifique.	Conductivité moléculaire.	Remarques.
15	0,06670	0,001285	19,27	
30	0,03335	0,000689	20,67	
60	0,01667	0,000393	23,58	
120	0,00834	0,000234	28,08	Solution trouble.
240	0,00417	0,000160	38 40	Solution opalescente.
480	0,00208	0,000103	49,44	Solution légèrement opalèscente.
960	0,00104	0,000057	54,72	Solution légèrement opalèscente.
1920	0,00052	0,000032	61,44	Solution légèrement opalèscente.

Dans le *tableau IV* nous voyons que la conductivité moléculaire éprouve un accroissement anormalement fort entre les dilutions de 30 et de 960 litres; et nous remarquons en outre que cette conductivité est en général très petite (jusqu'à la dilution de 240 litres elle reste même inférieure au coefficient que l'on préverrait pour le seul sodium, abstraction faite de tout ion négatif). Nous déduisons de là: 1° que l'équilibre règnant est plus ou moins de nature hydrolytique, et 2° que l'oléate dissous paraît être partiellement formé de groupements plurimoléculaires, au sein desquels la mobilité des ions, y compris le sodium, se trouve gravement entravée.

L'extraction par le toluol, pratiqués d'après notre procédé quantitatif, a pour effet d'augmenter la conductivité spécifique de la solution soumise au traitement. Voici par exemple les chiffres trouvés pour une solution d'une mole d'oléate sodique dans environ 60 litres d'eau: 0,000416 après sept jours de conservation, et 0,000506 après sept jours de contact avec un demi-volume de toluol. Voici également les chiffres trouvés pour une solution deux fois plus diluée: 0,000250 et 0,000423.

IV. Le mécanisme du dégraissage

Nous avons vu qu'une solution de savon, prise à une température convenable, peut céder au toluol une grande partie des on acide gras, tout en gardant la totalité de son alcali. Et nous savons également que le système diphasé ainsi constitué n'a besoin que d'être dûment agité pour qu'il se transforme en une émulsion non dépourvue de stabilité.

La persistance de cette émulsion n'est pas difficile à comprendre. Lorsque la solution toluique d'acide gras se trouve divisée en globules microscopiques, les molécules acides doivent avoir une tendance à occuper la surface de ces globules, c'est à dire la place où elles peuvent s'allier au toluol par leur volumineux groupement hydrocarboné tout en présentant à la phase aqueuse leur côté CO_2H. Les globules acquièrent ainsi un revêtement de fonctions acides, par lesquelles ils peuvent entretenir des rapports de salification (compliquée de dissociation et d'hydrolyse) avec l'alcali du liquide baignant. Et comme cet alcali forme l'objet d'une répartition régulière, et qu'il sollicite de toutes parts les globules émulsionnés, il n'est pas étonnant que ces derniers soient tenus à distance les uns des autres, et empêchés de se réunir en formations plus massives[1].

La même interprétation s'applique aux opérations de dégraissage, domestiques ou industrielles. Lorsqu'une huile ou une graisse, finement étendue à la surface de fibres animales ou de quelque autre objet, se trouve mise au contact d'une solution d'oléate de sodium, *la matière grasse agit à l'instar d'un liquide extracteur* et soutire de l'acide à la phase aqueuse. La friction mécanique aidant, la souillure peut alors se résoudre en particules globulaires ou autres, enrobées de fonctions acides, et très aptes à s'émulsionner dans une liqueur aqueuse plus ou moins alcaline[2].

Il arrive d'ailleurs fréquemment que la souillure à enlever soit rance, ou même constituée en grande partie par de l'acide gras libre. Elle est alors de par elle-même capable d'entrer en relations avec de l'eau alcalinisée, de sorte que le processus de la mise en émulsion se trouve réduit à sa forme la plus simple[3].

---

[1] L'acidité des globules fait naître de l'affinité chimique entre les deux phases de l'émulsion. Elle diminue, comme on dit, la tension superficielle au contact des liquides hétérogènes.

[2] A la température ordinaire l'huile d'olives, par exemple, est miscible avec l'acide oléique.—Cette même huile ne prend une quantité illimitée d'acide palmitique qu'au voisinage de 60°, et par le refroidissement elle laisse cristalliser la très grande partie de la matière dissoute. Aussi les opérations de dégraissage ne sont elles pas indépendantes de certaines conditions de température.

[3] Comparer: F. G. Donnan, *Zeitschrift für Phys. Chemie, 31*, 42; *Chem. Centralblatt 1900, I*, 243.

Nos recherches sur le pouvoir extracteur du toluol nous ramènent ainsi à la théorie déjà proprosée par Chevreul. et remise au point dans les publications de Krafft: *le dégraissage ne consiste pas essentiellement en une saponification sodique ou potassique des souillures grasses, mais en une simple mise en émulsion.*

L'expérience de tous les jours nous apprend qu'un savonnage n'est efficace qu'à la condition d'être mousseux. La coïncidence devient compréhensible lorsqu'on admet, conformément aux indications de notre chapitre III, qu'une solution de savon n'est apte à développer de la mousse que lorsque son acide gras jouit d'un degré suffisant de mobilité et d'extractibilité.—Il convient d'ailleurs de tenir compte également des considérations que l'on peut tirer de certain théorème de Gibbs (Thermodyn. stud. 271), développé ultérieurement par d'autres auteurs, notamment par H. Freundlich (Kapillarchemie, 50). Dans la mousse l'alcali doit se localiser de préférence dans l'épaisseur des lames liquides, tandis que l'acide gras doit tendre à s'étaler sur les surfaces libres. La souillure grasse soumise à l'action de la solution mousseuse trouve ainsi l'occasion de s'incorporer de l'acide qui s'offre, pour ainsi dire, spontanément à l'absorption.

SOLUBILITY IN CASES OF ALTERED SOLID PHASE

By Arthur Rindell
Helsingfors, Finland

The agricultural chemist is very often consulted on the availability of the plant food in fertilizers, soils and other substances. While it is agreed, that the useful effect of such substances depends upon their solubility, the problem is to determine the contents which possess a suitable solubility. The usual methods for this purpose are unfortunately quite incorrect, because they are founded on the erroneous conception, that different concentrations of acids have specific solvent action. Having devoted my investigations to the removal of this difficulty, I have met with several others concerning the application of the solution-theory.

Most of the materials in question contain chemical compounds subject to hydrolysis, such as phosphates and silicates. Especially when the kation is able to form slightly soluble salts of more basic nature than the original compound we have secondary reactions leading to the formation of new solids. Because we have to make a solubility determination, the original matter must be present in excess while here the solid phase becomes altered and increased from one to two or more.

The solvents used are either water or dilute acids, mineral or organic. Moreover the neutrality (resp. acidity) of the solvent is altered simultaneously with the change of the solid and in a very different manner, according to the solubility of the hydrolysis products. Since the secondary reactions produce basic solids, the solution tends to contain relatively more of the anion, or anions, and to show an acid reaction. This corresponds to the case of the hydrolysis of salts of feeble bases with strong acids.

It is obvious that these circumstances produce a peculiar course in the act of solution, when to the same amount of solvent are added increasing quantities of the solid. In the case of an ordinary solution the concentration increases as a rectilinear function of the added solid until saturation is reached and then remains constant. When the solid phase is altered, the dissolving power of the solvent is diminished not alone by the increased concentration of the dissolved part, but also through the alteration caused by hydrolysis, and the solution curve shows a slightly inflected form with concavity towards the axis of X. This presents a maximum from which the slope downwards is very gradual when more solid is added.

In such cases there is no definite saturation and it is not easy to represent the solubility by a definite number, especially since the secondarily formed solids are for the most part colloids, whose absorptive power and other properties are slowly altered and thus cause new complications.

It seems to me very inconvenient and disturbing to count these cases as solubility phenomena, and I might appeal to the congress to accept a special term for the dissolution equilibria, where the solid phase is altered by hydrolysis, as indicated above. I would propose the words *solvable* and *solvability* in English, *lösbar* and *Lösbarkeit* in German and *solvable* and *solvabilité* in French.

Perhaps it is necessary to point out that this peculiar kind of equilibrium is of importance not only to the agricultural chemist. Important series of investigations concerning somewhat similar cases are shown for instance in papers of *C. Hoitsema*[1] on mercuric sulphate, of *G. Rutten*[2] and of *W. Hertz* and *A. Bulla*[3] on the nitrate of bismuth, of *J. M. van Bemmelen*[4] on the trichloride of antimony, and of *A. J. Cox*[5] on the chromates of mercury, bismuth and lead.

---

[1] Zeitschr. f. physikal. Chemie *17*, 651.
[2] Zeitschr. f. anorgan. Chemie *30*, 342.
[3] Zeitschr. f. anorgan. Chemie *61*, 387.
[4] Zeitschr. f. anorgan. Chemie *33*, 272.
[5] Zeitschr. f. anorgan. Chemie *50*, 226.

ON MIXED CRYSTALS OF POTASSIUM AND AMMONIUM CHLORIDES

BY KENJIRO UYEDA

College of Science and Engineering, Kyoto Imperial University

The formation of the mixed crystals of potassium and ammonium chlorides was first observed by Chevreul[1] and Knopp.[2] Their study was later taken up by Krickmeyer[3] who has shown among other things that their mutual solubilities are limited, and, further, Fock[4] has found a gap in their mutual solubilities at 25°, lying at about 18 to 99 mol. per cent ammonium chloride. At the suggestion of Professor Y. Osaka, I have been engaged in the further study of these mixed crystals, and the results are here briefly described.

The chlorides were purified by the repeated recrystallization, the flasks well steamed and the measuring apparatus carefully calibrated. Determination of the solubilities were made at 25.0°, 65.0° and 90.0°, the temperature in each case having been kept constant within 0.05°. They were conducted in the following way. Into an Erlenmeyer flask of about 25 c.c. capacity, about 5 grams of distilled water and sufficient quantities of the chlorides (in different proportions for the several determinations) were introduced, and the flask was closed with an India rubber stopper tightly covered, together with the neck of the flask, with a sheet of oil paper. It was shaken in a thermostat for a day and night, and then left to stand still. When the suspended matter settled down at the bottom of the flask, about 2 cc. of the clear solution were taken out and weighed, then diluted to 100 cc. with distilled water and subjected to analysis.

Ten cc. of the diluted solution were titrated for chlorine with decinormal silver nitrate solution using potassium chromate as an indicator. Ten cc. of the same solution were again taken

---

[1] Compt. rend., *85*, 493 (1877).
[2] Molekularkonstitution und Wachstum der Kristalle, Leipzig, 1867.
[3] Zeit. f. physik. Chem., *21*, 53 (1896).
[4] Zeit. f. Kristall., *28*, 337 (1897).

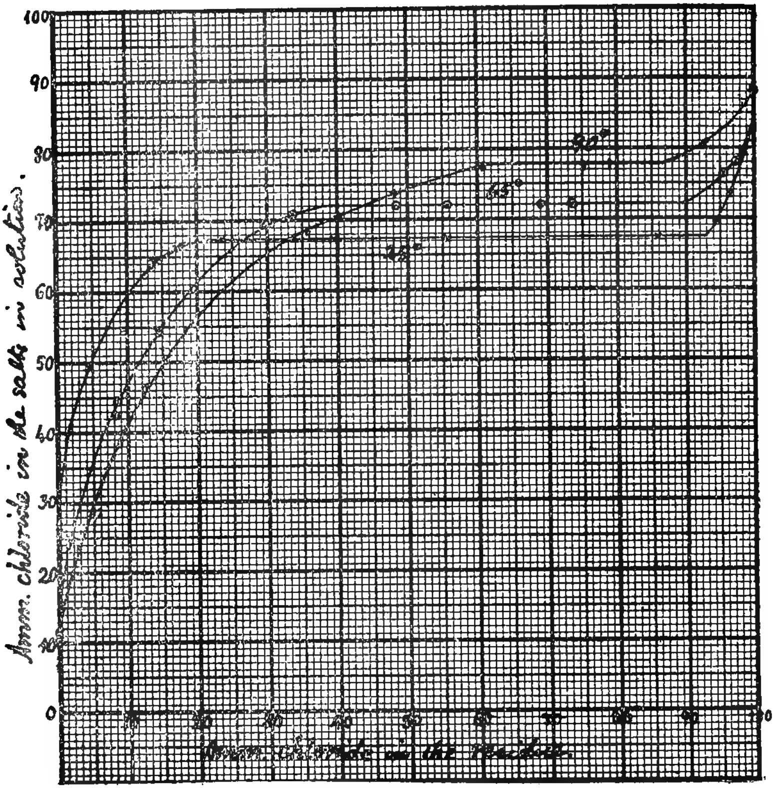


FIGURE I

in an Erlenmeyer flask of about 100 cc. capacity, and 20 cc. of the decinormal caustic potash solution were added. A small glass funnel was set at the mouth of the flask to prevent the loss of the liquid which was kept gently boiling, in order to expel ammonia completely from the solution. The latter was then allowed to cool, titrated for the free alkali with decinormal hydrochloric acid, and the amount of ammonium chloride calculated. From the amount of the total chlorine and of the ammonium salt, that of potassium chloride was estimated. The residue in the flask was analysed in the same way.

The results are given in the following table, and graphically shown in Fig. I.

25.0°		65.0°		90.0°	
I	II	I	II	I	II
10.4	0.	11.6	0.	23.7	2.7
26.9	0.	25.0	1.6	31.0	6.0
49.7	4.5	42.8	8.1	39.0	9.0
64.3	14.0	44.3	8.3	46.5	12.4
66.1	17.0	54.2	14.2	68.3	35.6
67.4	23.5	69.3	29.9	70.4	40.1
67.2	39.5	70.7	33.7	73.8	48.1
67.2	55.5	72.0	48.1	77.4	60.8
67.3	85.9	72.0	55.8	77.8	75.1
69.6	94.7	72.0	69.0	77.8	79.0
73.2	96.3	72.2	73.4	80.6	92.9
84.2	100.0	76.5	95.5	86.1	98.8
		77.9	97.3	88.8	100.0
		79.4	98.4		
		88.1	100.0		

In the table, the numbers in Column I represent in each case the gram percentage of ammonium chloride in the salts in solution, and those in Column II the gram percentage of the same salt in the residue.

From these results the following conclusions may be drawn:

I. The mutual solubilities of potassium and ammonium chlorides increase as temperature rises.

II. The solubility of ammonium chloride in potassium chloride increases with the temperature much more rapidly than that of potassium chloride in ammonium chloride.

III. The mixed crystals have the following gaps:

Temperature	Gram Percentage of Amm. Chloride	Molar Percentage of Amm. Chloride
25°.0	21-93	27-95
65°.0	38-90	46-93
90°.0	62-87	69-90

Abstract

EQUILIBRIUM IN THE SYSTEM OF SULPHURIC ACID, SULPHATE OF AMMONIA AND SULPHATE OF LITHIUM AT .30°C.

By Dr G. C. A. van Dorp
Katwijk aan Zee, Holland

The ordinary graphical figure in the equilateral triangle, scale one mm. for one per cent was not exact enough to elucidate the results of the analyses. The use of three perpendicular axes was necessary and a larger scale.

Besides the already known combinations of one mol. sulphuric acid to one mol. sulphate of ammonia and of one mol. sulphuric acid to one mol. sulphate of lithium I found three, as far as I know, as yet unknown combinations: 4 mol. sulphuric acid on three mol. sulphate of ammonia on one mol. sulphate of lithium; 4 mol. sulphuric acid on two mol. sulphate of ammonia on 2 mol. sulphate of lithium; 4 mol. sulphuric acid on 1 sulphate of ammonia on three sulphate of lithium. So the sum of the mol. in a combination in these three cases was found to be eight, which suggested the hypothesis that at 30° Celsius the combination possible with these components, also with less sulphuric acid were combinations of eight mol., a hypothesis which afterwards proved successful.

ON THE DETERMINATION OF THE WORTH OF TANNING MATERIAL, SPECIALLY FOR TANNING FISHING NETS

By Dr. G. C. A. van Dorp

Katwijk aan Zee, Holland

In the "Gedenkboek," offered to the late Dr. van Bemmelen, my highly esteemed initiator into the beauty of chemistry, and one of the founders of the colloid-chemistry, I published something of the above-named matter.

There had been sold at Katwijk a large fishing place at the Dutch coast, a tanning material which on hidepowder gave a better analysis than the ordinary cachou, and yet gave for the tanning of fishing nets very bad results. I then tried the adsorbing power of cotton for cachou and the other material (probably mangrove-extract) and found that cotton shaken with solutions of the first adsorbed a great deal of it, that of the second nearly nothing was adsorbed. This induced me to use no longer alone the hidepowder method, but also to determine the adsorbing power on cotton. I then used the same solution that had been used with the hidepowder and calculated the tanning worth in proportion to a standard material. This was but a preliminary method, as I did not doubt that the tanning material was not chemically bound by the cotton, but adsorbed according to the laws of adsorption. In this case there were two really exact methods, the first to determine once for all what under given conditions could be adsorbed out of a given solution of the standard material, and to determine in each case, how strong a solution of the material that was to be examined, ought to be to give the same adsorption. It was evident that in this manner as a rule more than one experiment was due, the first to know the probable strength of the solution, the second to try if this was really the right strength. Another method seemed to be to construct an adsorbing curve of the standard material. This curve once constructed, and the adsorption determined out of any solution of the material that had to be examined we could find in the curve the solution in the standard that would give the same adsorption, and so determine the value of the examined material.

So I resolved to determine such an adsorption-curve. This would have still more advantages, it would make me better acquainted with many of the properties of the procédé, which it was always good to know, and perhaps this knowledge would teach me the faults of the method, and the way how to diminish them. This proved true. First when starting from solutions of 7 gr. per L. I had hardly any difficulties, but when using a solution of 70 gr. per L. it appeared very difficult to determine what was adsorbed. The titration after Löwenthal was not well possible with the very colored solutions, and to dry such concentrated solutions into constant weight proved very difficult. In the drying over it was impossible at 100 centigrade, but at 103 centigrade it was possible, when the temperature was very exactly regulated to dry into constant weight. It was still better to dry in the vacuum at 100 centigrade. This strongly confirmed the truth asserted by those who, of late, advised to dry in the vacuum when using the official method of tanning analysis.

But even when drying in the vacuum constant adsorbing values were not found. It proved impossible to bring the adsorption to the end with shaking only. The solution decanted after half an hour's shaking from the cotton, and that pressed out of it, differed too much, shaking for a longer time would give no improvement. I then took refuge to a combination of shaking and pressing, at a fixed temperature, in wide-mouthed flasks, with an apparatus, reminding one of the old-fashioned Dutch churn. Thus I got results that agreed well with each other, when shaking for 5 minutes, pressing 2½ minutes, and repeating this three times. After this the mass would stand still, so that the foam could settle. Altogether the treatment would last three-quarters of an hour. To avoid differences, proceeding from differences in the preparation of the solution, it is recommendable to begin by making a very strong solution, out of which the more diluted are made.

In this way with my standard cachou I got the data given in Table I, with which the diagram was constructed. Now I must confess that this curve is not a real scientific, adsorption-curve.

Mathematical considerations, which to tell would take too long here, convinced me that it was impossible to test this curve on the adsorption formula, $\frac{K}{M} = kc^{\frac{1}{n}}$, this is only possible with solutions of chemically pure material, but I think that for my purpose the curve is very good. It is true that even so we cannot know how much real tanning material there is in a given solution (the adsorption being as is known, too much influenced by different additions), but we will know how much of it will be bound by the nets, and this is in the first instance the thing we want to know. Whether this method will also be of importance for the examination of tanning material used in leather manufacture is a thing I don't know, but I suppose it is worth trying.

Solved per Liter	Soluble in 50 c.c.		Rest in 50 cc. after 100 cc. was churned with 10 g.r. Cotton (corrected for the soluble part of the Cotton)	Adsorbed by Cotton
	Determined	Calculated		
70. gram	2.3670		2.1925	0.1745
49. gram	1.6604	1.6569	1.5013	0.1556
34.3 gram		1.1568	1.0307	0.129
27.4 gram	0.9286	0.9278	0.8173	0.1105
19.21 gram		0.6494	0.5663	0.0831
15.37 gram	0.5204	0.5195	0.4493	0.0702
10.76 gram		0.3636	0.3065	0.0571
8.61 gram		0.2908	0.2411	0.0497
6.88 gram		0.2326	0.1864	0.0462
4.81 gram		0.1628	0.1347	0.0281
3.85 gram	0.129	0.1302	0.1123	0.0179

DIE PRUFUNG VON LABORATORIUMTHERMOMETERN

GEHEIMER REGIERUNGSRAT PROF. DR. WISBE
Charlottenburg

Das Glasthermometer, besonders in seiner gebräuchlichsten Form als Quecksilberthermometer ist für den Chemiker eines der wichtigsten Hilfsinstrumente sowohl im Laboratorium wie im Fabrikbetriebe. Die Genauigkeit der Thermometer ist aber keine absolute, sondern nur eine relative, da es fast unmöglich ist, ein ganz fehlerfreies Thermometer herzustellen. Sie bedürfen daher stets einer Korrektionstabelle. Ausserdem unterliegt das Glasthermometer, wie viele andere Jnstrumente, beim Gebrauch Veränderungen, die von Zeit zu Zeit seine Nachprüfung nötig machen.

Der Chemiker ist aber meist nicht in der Lage, seine Thermometer selbst zu kontrollieren, auch stehen ihm die Erfahrungen, welche zu einer sachgemässen Prüfung nötig sind, in der Regel nicht zu Gebote.

Es ist daher von grossem Wert für den Chemiker, dass eine Reihe von staatlichen Anstalten bestehen, die sich mit der Prüfung von Thermometern befassen. Hierbei muss in erster Linie der Physikalisch-Technischen Reichsanstalt in Charlottenburg gedacht werden, da sie diejenige Anstalt ist, die sich am längsten und in umfangreichster Weise damit beschäftigt. Auch hat die Reichsanstalt ähnlichen Jnstituten in anderen Ländern in vielen Beziehungen zum Vorbilde gedient. Von den Anstalten in anderen Ländern seien nur die bekannteren aufgezählt, das Bureau of Standards in Washington, das National Physical Laboratory in Teddington und das Laboratoire d'Essais in Paris.

Diese Jnstitute haben für die Prüfung von Thermometern besondere Vorschriften herausgegeben, von denen die der Reichsanstalt die ältesten sind und die den Vorschriften der übrigen Länder als Vorbild gedient haben. Jn Deutschland befasst sich auch die unter Aufsicht der Reichsanstalt stehende Grossherzolich Sächsische Prüfungsanstalt in Jlmenau mit der Prüfung von

Laboratoriumthermometern. Jch will mich darauf beschränken, auf Grund der deutschen Prüfungsbestimmungen kurz die hauptsächlichsten Anforderungen anzugeben, die bei der Prüfung von Thermometern an letztere zu stellen sind und zwar mit besonderer Berücksichtigung der Laboratoriumthermometer.

Eine der wichtigsten Fragen für die Güte eines Thermometers ist die Beschaffenheit des Glases sowohl in chemischer wie in physikalischer Beziehung. Das Glas hat, wie viele andere Körper, die Eigenschaft der thermischen Nachwirkung, die sich durch das Ansteigen des Eispunktes bei neuen Thermometern dokumentiert. Man kann dieses jahrelang andauernde Ansteigen des Eispunktes vermeiden, wenn das Thermometer vor der Herstellung seiner Teilung einer künstlichen Alterungsverfahren unterzogen wird, das in einer 8 bis 10-tägigen Erhitzung des Thermometers auf einer Temperatur besteht, die der Erweichungstemperatur des Glases nahe kommt. Nach der Erhitzung muss eine möglichst langsame Abkühlung des Thermometers erfolgen.

Ein solchermassen behandeltes Thermometer erfährt bei nachherigem Gebrauch keine weitere Erhöhung, wohl aber nach jeder Erhitzung eine kleine vorübergehende Erniedrigung, eine Depression des Eispunktes, deren Grösse von der Höhe der Temperatur und von der chemischen Zusammensetzung des Glases abhängt. Glassorten, welche Kali und Natron enthalten, weisen grosse Depressionen auf, diejenigen mit nur *einem* Alkali kleine. Von den zur Herstellung besserer Thermometer bekannten Glassorten zeichnen sich die Jenaer Thermometergläser durch besonders kleine Nachwirkungen aus. Thermometer aus dem Jenaer Normal-Thermometerglas 16^{III} zeigen nach Erwärmung auf 100° nur eine Depression von 0,05 bis 0,07° C. solche aus Jenaer Borosilikatglas 59^{III} oder aus Jenaer Verbrennungsröhrenglas nur 0,02°.

Die Prüfung der Thermometer zerfällt in zwei Teile, die Vorprüfung und die Hauptprüfung. Erstere erstreckt sich auf die ordnungsmässige Herstellung des Thermometers, während letztere die eigentliche thermometrische Untersuchung umfasst.

Bei der Vorprüfung wird nachgesehen, ob die Kapillarröhre rein ist und ein gleichmäissg verlaufendes Kaliber hat. Am oberen Ende der Kapillare soll eine birnförmige Erweiterung angeblasen sein, um abgetrenntes Quecksilber leichter zu vereinigen und ein Zersprengen des Thermometers bei Ueberhitzung zu verhüten. Das Quecksilber muss rein und trocken sein, so dass beim Zurückgehen des Fadens an keiner Stelle der Kapillare sich Teilchen von ihm abtrennen.

Thermometer für Temperaturmessungen über 280° C. müssen oberhalb des Quecksilbers mit einem trockenen Gase (Stickstoff, Kohlensäure) von entsprechendem Drucke gefüllt sein, um das Quecksilber am Sieden zu hindern.

Die Skalenteilung soll ohne augenfällige Einteilungsfehler in dauerhafter Weise ausgeführt sein. Die Teilstriche sollen senkrecht zur Achse des Thermometers stehen. Besonderer Wert ist auf eine deutliche Bezifferung der Skala zu legen.

Die Hauptprüfung beginnt mit einer mindestens achttägigen Beobachtung der Thermometer hinsichtlich der Unveränderlichkeit ihrer Angaben durch Eispunktsbestimmungen oder dergl.

Die weitere Prüfung erfolgt sodann, je nach der Beschaffenheit der zu prüfenden Jnstrumente entweder durch eine Bestimmung des Fundamentalabstandes, durch Kalibrierung und Vergleichung mit Normalthermometern oder nur durch Vergleichung mit Normalthermometern in Temperaturbädern.

Als Temperaturskala wird allgemein die hundertteilige internationale Wasserstoffskala zu Grunde gelegt, die mit der thermodynamischen Skala fast identisch ist. Leider ist man bis jetzt nur zu einer Vereinbarung zwischen 0 und 100° gekommen, für höhere Temperaturen besteht noch keine vollkommene Einheitlichkeit. Es ist aber wenigstens so viel erreicht, dass man z.B. für den Siedepunkt des Schwefels, der bei thermometrischen Arbeiten auch als Fixpunkt benutzt wird, die Temperatur 444,7° C angenommen hat, die wahrscheinlich bis auf weniger als 0,1° mit der thermodynamischen Skala übereinstimmt.

Bei der fundamentalen Prüfung eines Thermometers sind auch die s.g. Gasreduktionen zu berücksichtigen. Jedes Glasthermometer zeigt die Temperatur in seiner individuellen Skala an, die von der Skala des Gasthermometers je nach der Art des Glases verschieden abweicht. Für die bekannteren Glasarten sind die Abweichungen ein für alle Mal durch umfangreiche Vergleichungen mit dem Gasthermometer bestimmt worden, so dass es leicht ist, die Angaben aller Glasthermometer auf dasselbe einheitliche Mass zurückzuführen.

Die zweite Art der Prüfung ist einfacher und geschieht durch Vergleichung in Temperaturbädern mit Normalthermometern, die an das Gasthermometer angeschlossen sind. Zur Vergleichung werden Flüssigkeits-oder Dampfbäder benutzt, für tiefe Temperaturen flüssige Luft sowie Gemische aus Salzen mit Eis oder aus Alkohol mit fester Kohlensäure.

Die Prüfung der Thermometer erfolgt im Allgemeinen so, dass die ermittelten Korrektionen sich auf ganz eintauchender Faden beziehen; auf Wunsch kann jedoch das Thermometer für eine bestimmte Eintauchtiefe geprüft werden; es ist in diesem Falle die mittlere Temperatur des herausragenden Fadens beim Gebrauch des Thermometers anzugeben.

Für die verschiedenen Gattungen von Thermometern sind bestimmte Fehlergrenzen vorgeschrieben, bei deren Einhaltung die Thermometer einen amtlichen Stempel als Kennzeicher der vollzogenen Prüfung und einen Prüfungsschein erhalten, in dem die ermittelten Korrektionen angegeben sind. Die Genauigkeit in den Angaben der Korrektionen richtet sich nach der Beschaffenheit der Jnstrumente und dem Ausfall der Prüfung und kann in sehr weiten Grenzen schwanken. Für Laboratoriumthermometer werden die Korrektionen in der Regel auf 0,1° C. bei hochgradigen Thermometern auf halbe oder ganze Grade abgerundet.

Diese wenigen Andeutungen mögen genügen, um zu zeigen, welch' grosse Mühe mit der sachgemässen Prüfung von Thermometern verbunden ist, zugleich aber auch, wie notwendig eine solche Prüfung ist, wenn es sich darum handelt, genaue Temperaturmessungen auszuführen. Jn Deutschland sind im vorigen Jahre 110000 Thermometer amtlich geprüft worden, unter denen sich über 7000 Laboratorium—und ähnliche Thermometer befanden, darunter allein 2000 hochgradige, zum Teil mit Temperaturangaben bis 575° C. Für die anderen Länder stehen mir die Zahlen nicht zur Verfügung, allein ich zweifle nicht, dass sie auch eine erklekliche Höhe erreichen. Eine besondere Genugtuung gewährt dabei die Gewissheit, dass durch die amtlichen Prüfungen dieser Thermometer in den verschiedenen Staaten nach gleichartigen Grundsätzen die Einheitlichkeit in den Temperaturangaben für alle geprüften Thermometer, besonders für die Laboratoriumthermometer, gewährleistet ist.

Schliesslich möge darauf hingewiesen werden, in welcher Weise die Verwendung ungeprüfter oder fehlerhafter Thermometer die Genauigkeit der Untersuchung beeinträchtigen kann. So ist z.B. bei der Bestimmung der Dichte mit Pyknometern eine Genauigkeit der Temperaturbestimmung auf 0,1° C. unerlässlich, um die dritte oder vierte Dezimale sicher zu erhalten. Bei feineren polarimetrischen Untersuchungen muss die Temperatur der zu untersuchenden Lösung mit mindestens der gleichen Genauigkeit bekannt sein. Auch dürften die grossen Abweichungen bei den in der Litteratur angegebenen Schmelzund Siedepunkten sich zum grossen Teil durch Verwendung fehlerhafter Thermometer erklären lassen.

THE SYSTEM OXALIC ACID, OXALATE OF AMMONIUM AND WATER AT 30° AND 45°

By H. W. Woudstra
Helder, Holland

We know three well-defined ammonium salts of oxalic acid:

1e. The neutral oxalate $(COONH_4)_2.H_2O$
2e. The acid oxalate $(COO)_2$ $H.NH_4H_2O$
3e. The quadroxalate $(COOH)_2(COO)_2$ $H.NH_4.2$ H_2O

The first crystallizes in long prisms, which are rhombic, hemiedric. Its solubility after Engel[1] is 2,215 grams in 100 grams water. On heating a solution of this salt in an open vessel ammonia is said to escape and prolonged boiling will leave behind a solution of pure oxalic acid (Gillot[2]).

The acid oxalate, too, crystallizes in rhombic crystals. The solubility of these salts has been determined with only moderated precaution as to constancy of temperature by William Ripley Nichols.[3]

In hundred grams of water of 15° dissolve 4.22 grams of the neutral oxalate; at 11°5, 100 grams of water dissolve 6.26 grams of the acid oxalate. The solid salt in equilibrium with the saturated solution at 11°5 has after Nichols the composition of the pure acid oxalate.

This last result does not agree with the experiments of Engel[4], who declares not to be able to determine the solubility of acid oxalate because this salt decomposes in solution into quadroxalate and neutral oxalate. The first salt separates from saturated solution of the acid oxalate. He worked at 0°.

The solubility of the quadroxalate, which crystallizes in the triklinic system as determined by Nichols, amounts to 1.81 grams in 100 grams water.

In this paper I have studied the equilibria, which occur when mixtures of oxalic acid and ammonium-oxalate in different proportions are shaken with water at constant temperatures in a thermostat. The temperature of the thermostat was kept nearly constant within 0.1° by means of a toluol-thermo-regulator. The well-stoppered flasks contained in most cases weighed quantities of the three components, water, oxalic acid and neutral oxalates. Equilibrium was reached within 2-10 days; each day the flasks were shaken for about 6-8 hours by means of a hot-air-motor which turned the axle in the thermostat, on which the flasks were fixed.

---

[1] R. Engel. Comptes Rendus d. l'Acad. d. Sc. d. Paris, 102, 365.
[2] Gillot. Bulletin Acad. Roy. Belg. 1900, 744.
[3] W. R. Nichols. Chem. Nem. Vol. 21-22, p. 244, 1870.
[4] l.c.

The composition of a solution, which was in equilibrium with the solid phase, was determined in the following manner: a weighed quantity of the solution was titrated with chamæleon solution after addition of sulphuric acid, the total amount of oxalic acid in this way being estimated. Another weighed quantity was distillated with kalium-hydroxide; the ammonia set free was titrated with hydrochloric acid and bariumhydroxide.

The compositions of the solutions are given in Table I under B in percentages of anhydrous free oxalic acid, and neutral ammonium-oxalate for the temperature of 30°. Under A the compositions of the initial mixtures of water, oxalic acid and ammonium-oxalate are indicated in the same way.

Table II contains these compositions for a temperature of 45°. Fig. I represents the results of Table II graphically. The corners of the equilateral triangle A B C represent, respectively, water, anhydrous neutral. oxalate and anhydrous oxalic acid. Each point within the triangle represents a mixture of these three components. The percentages are given by the distances of the point from the sides of the triangle, measured along lines parallel to the sides. To find the composition of the mixture represented by point E, f. i. we draw a line parallel to A C or B C. The distance of E from A B measured along one of these lines is equal to the percentage of anhydrous oxalic acid.

In the same way by drawing a line through E parallel to A C or B C, the distance of E from A C, measured along one of these lines represents the percentage of anhydrous oxalate.

The point E represents the quadroxalate, F the acid oxalate, G the neutral oxalate. The oxalic acid is represented by the point D on the side A C.

The isotherm at 45° MHIKL consists of four branches corresponding with the solid phases $(COOH)_2.2_2H_2O$, $(COOH)_2.(COO)_2$, $H.NH_4.2\ H_2O$, $(COO)_2\ H.NH_4.H_2O$ and $(COONH_4)_2.H_2O$. The solutions represented by the points of these four branches are respectively in equilibrium with these substances.

All points in the area AMHIKL represent unsaturated solutions; all points in the area MHIKL.BC supersaturated solutions, which decompose in saturated solution and solid phase.

The point N_1, f.i. represents such an unstable system, which separates into quadroxalate and the solution represented by the point N. The point which represents the solution in equilibrium with the solid phase is found by drawing a line through the points which represent the solid phase and the unstable system.

If the composition of two solutions in equilibrium with the same solid phase and the compositions of the unstable systems, which separated into these solutions and this solid phase, is known, the composition of the solid phase may be found by drawing lines through the points which represent the solution and the corresponding initial unstable system. The point of intersection of these lines represents the composition of the solid phase.

We see from the shape of the isotherm, that on adding neutral oxalate to the saturated solution of oxalic acid the concentration of the solution at first slightly increases; soon, however, tetraoxalate separates; the solution decreases constantly its amount of dissolved substances. As soon as the composition of the solution corresponds with a saturated solution of quadroxalate the concentration of the solution increases on further addition of neutral oxalate.

The solubility of the quadroxalate may be graphically determined by drawing the line E A. Its point of intersection with the isotherm represents the saturated solution of this salt. In this way we find for the composition of this solution: 3% anhydrous oxalate of ammonium and 6.3% anhydrous oxalic acid.

The amount of dissolved quadroxalate calculated from these data are respectively: 11.27% and 10.97%; mean, 11.12%. At 45° the saturated solution of quadroxalate of ammonium contains 11.12% $(COOH)_2\ (COO)_2\ H.NH_4.2\ H_2O$.

From the isotherm at 30°, which may be constructed after

Table I we deduce, graphically, that the saturated solution of quadroxalate at 30° contains 2% ammonium oxalate and 4% oxalic acid, which corresponds respectively with 7.52% and 6.90% quadroxalate; mean, 7.21%. The isotherm at 30° resembles very closely that at 45°.

On further increasing the amount of neutral oxalate the point I is reached. This —————————— is a second tripelpoint, where solution, quadroxalate and acid oxalate coexist. This point falls at 45° and at 30° exactly on the line F A, which confirms the experiments of Engel. It is impossible to prepare a saturated solution of acid oxalate in equilibrium with pure acid oxalate. Some quadroxalate will always separate from the solution.

The solutions in equilibrium with pure acid oxalate contain more oxalate of ammonium than the saturated solution of acid oxalate. Their concentration increases gradually till the third tripelpoint K is reached. Here neutral oxalate separates. The solutions in equilibrium with neutral oxalate gradually decrease in concentration on further addition of neutral ammonium oxalate. When we begin with a saturated solution of this salt and add oxalic acid the concentration of the solution increases; more neutral oxalate goes into solution.

ABSTRACT

In this I determined:

1e. The isotherms of the system ammonium oxalate, oxalic acid and water at 30° (cor) and at 45° (corr);

2e. The solubility of oxalic acid at 30° and 45° respectively, 12.59 and 21.015 grams in 100 gram solution;

3e. The solubility of neutral ammonium oxalate at 30° and 45°, respectively, 5.53 grams and 8.3 grams in 100 gram solution;

4e. I proved that a saturated solution of acid ammonium oxalate deposes at 30° and at 45° quadroxalate of ammonium;

5e. I determined the solubility of quadroxalate graphically at 7.21 grams in 100 gram solution at 30° and at 11.12 grams in 100 gram solution at 45°.

TABLE I

A		B		Solid phase
Oxalate of Ammonium	**Oxalic Acid**	**Oxalate of Ammonium**	**Oxalic Acid**	
0.13%	20.58%	0.14 %	12.36 %	Oxalic acid
1.79%	18.27%	0.28 %	12.775%	id. + Tetra-oxalate
1.46%	19.48%	0.28 %	12.775%	id. id.
1.88%	20.31%	0.28 %	12.95 %	id. id.
0.27%	22.32%	0.285%	12.345%	id. id.
0.71%	19.42%	0.29 %	12.68 %	id. id.
0.97%	19.72%	0.29 %	12.74 %	id. id.
0.48%	19.76%	0.29 %	12.68 %	id. id.
1.37%	20.12%	0.29 %	12.51 %	id. id.
2.00%	19.28%	0.30 %	12.81 %	id. id.
0.37%	20.28%	0.30 %	12.71 %	id. id.
0.68%	11.11%	0.37 %	10.46 %	Tetra-oxalate of Ammonium
....	....	0.43 %	11.44 %	id.
1.13%	9.26%	0.47 %	8.87 %	id.
0.83%	16.30%	0.97 %	11.36 %	id.
10.03%	24.07%	0.91 %	5.65 %	id.
....	....	1.14 %	4.65 %	id.
....	....	3.60 %	3.55 %	id.
10.80%	20.67%	5.91 %	4.00 %	id.
....	....	5.96 %	4.17 %	Tetra-oxalate+hydro-oxalate
....	....	5.98 %	4.17 %	id.
13.87%	15.86%	5.98 %	4.23 %	id.
17.28%	14.10%	6.00 %	4.25 %	id.
....	....	6.21 %	4.08 %	Acid-oxalate
....	....	6.785%	3.56 %	id.
....	....	6.73 %	3.82 %	id.
....	....	6.015%	3.96 %	id.
26.38%	5.10%	8.19 %	3.36 %	Acid-oxalate+neutral oxalate
27.65%	4.28%	8.20 %	3.06 %	id.
20.37%	11.90%	8.24 %	3.31 %	id.
....	....	8.26 %	3.41 %	id.
23.38%	9.60%	8.27 %	3.49 %	id.
....	....	8.30 %	3.39 %	id.
24.14%	7.23%	8.32 %	3.22 %	id.
32.03%	2.75%	8.34 %	3.32 %	id.
27.28%	3.55%	8.36 %	3.30 %	id.
....	....	8.36 %	3.04 %	id.
20.37%	11.90%	8.40 %	3.34 %	id.
25.81%	7.53%	8.51 %	3.22 %	id.
....	....	8.52 %	3.25 %	id.
....	....	8.63 %	3.20 %	id.
....	....	7.40 %	2.76 %	Neutral oxalate
....	....	5.53 %	0.22 %	id.

TABLE II

A		B		
Oxalate of Ammonium	Oxalic Acid	Oxalate of Ammonium	Oxalic Acid	Solid Phase
....	....	....	21.01%	
....	....	....	21.02%	Oxalic acid
....	....	0.22%	21.22%	id.
....	....	0.25%	21.09%	id.
....	....	0.27%	21.22%	id.
0.24%	24.93%	0.27%	21.21%	id.
....	....	0.30%	21.32%	id.
....	....	0.31%	21.31%	id.
....	....	0.53%	20.73%	Oxalic acid and Tetra-oxalate
1.97%	23.63%	0.53%	21.44%	id.
....	....	0.53%	21.38%	id.
....	....	0.53%	21.46%	id.
....	....	0.53%	21.50%	id.
1.94%	26.39%	0.53%	21.30%	id.
0.65%	26.23%	0.54%	21.35%	id.
1.27%	24.24%	0.56%	21.23%	Tetra-oxalate
....	....	0.61%	20.55%	id.
2.58%	23.13%	0.54%	20.92%	id.
....	....	0.51%	20.88%	id.
3.91%	21.33%	0.79%	16.44%	id.
6.48%	21.22%	1.23%	12.28%	id.
9.46%	22.18%	2.16%	7.98%	id.
9.59%	24.37%	3.54%	5.83%	id.
11.08%	19.02%	5.65%	5.67%	id.
11.55%	18.56%	6.72%	5.95%	id.
13.46%	17.40%	8.77%	6.69%	Tetra-oxalate + acid-oxalate
15.12%	14.46%	8.72%	6.37%	id.
17.76%	12.63%	8.93%	6.27%	Acid-oxalate
16.00%	11.00%	9.04%	6.14%	id.
....	....	12.40%	4.97%	Acid-oxalate + neutral oxalate
23.32%	6.36%	12.27%	5.00%	id.
19.83%	7.93%	12.28%	5.02%	id.
19.99%	10.00%	12.37%	5.01%	id.
25.19%	2.64%	8.31%	3.04%	Neutral oxalate
25.00%	0.98%	9.59%	1.45%	id.

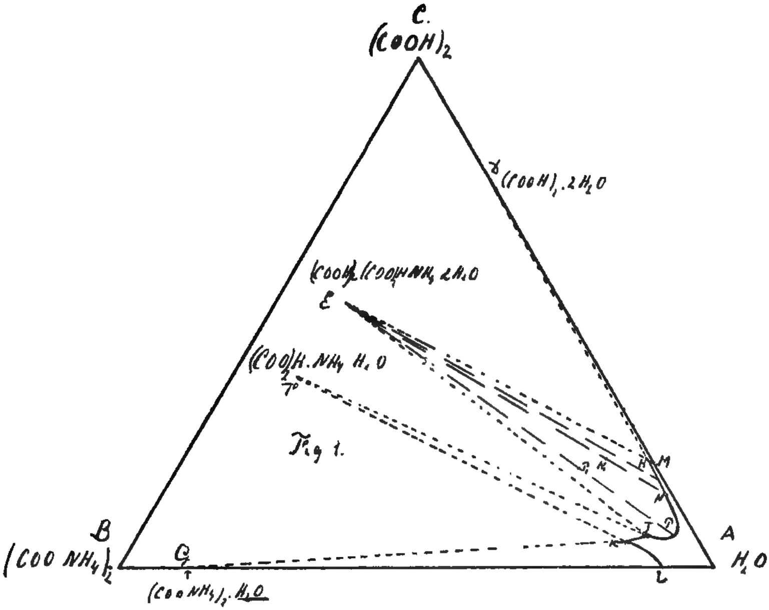

C.
(COOH)₂
D (COOH)₂.2H₂O
(COOH)₂(COO)₂HNH₄ 2H₂O
E
(COO)₂H.NH₄ H₂O
7°
Fig 1.
H
M
K
N
T
I
K
A
H₂O
B
(COO NH₄)₂
G
(COONH₄)₂.H₂O
L

FIGURE 1

Abstract

STUDIES ON THE CHEMICAL KINETICS OF CATALASE

By Eiichi Yamasaki

The Chemical Institute of the Science College, Imperial University of Tokyo

The chemical kinetics of this important enzyme is complicated by the fact that it is destroyed with considerable rapidity in the presence of the substrutum, hydrogen peroxide. But as this substance can be measured with great ease and accuracy and the enzyme of well defined qualities can be readily obtained, the more detailed study of the subject seemed to afford a promising opening for kinetic investigation of the more complicated enzyme actions. According to Prof. Ikeda the course of decomposition of hydrogen peroxide by catalase can be described by the following extremely simple equations:

$$\frac{dc}{dt} = -kEc \quad (a) \qquad \frac{dE}{dt} = -k'Ec \quad (b)$$

where c represent the concentration of the peroxide, E that of the enzyme, t time, and k and k′ the velocity coefficients. The author undertook the verification of these equations and was able confirm all the deductions experimentally. The enzyme employed in the experiments described in this paper was obtained from young shoots of bamboos, *Phyllotachys mitis, Riv.* The conditions of the experiment were varied with respect to temperature and concentrations of the substrutum and the enzyme. In all thirty four courses of the reaction were measured and calculated.

From (a) and (b) the following relation is obtained by integration and transformation;

$$v = k'(A + c) \qquad (c)$$

where v stands for the relative velocity of the reaction and A for

$$\left(\frac{k}{k'}E_0 - C_0\right); \quad E_0 \text{ and } C_0$$

being the initial concentrations of the enzyme and the substrutum respectively. V was calculated directly from the experimental data. On plotting the relation between v and c in a diagram, it was found that all the points belonging to a single course of the reaction lie on a straight line, and that all the lines pertaining to one and the same temperature are parallel to one another. In this way equation (c) was directly verified and (a) and (b) indirectly. By the graphical construction approximate values of k′ and A were obtained. The more exact values were then calculated by successive approximation from the integrated equation,

$$\ln\frac{C_0}{C} - \ln\frac{C_0 + A}{C + A} = k'At$$

The determination of k′ in this way seems to be tolerably accurate, because all the values for the same temperature agree remarkably well among themselves. On the contrary, the values of kE_0 calculated from that of A are not so concordant. But the proportionality between kE_0 and the amount of the enzyme taken for the experiment was established beyond a doubt.

As a pure enzyme is an unknown thing, the concentration of an enzyme must always be expressed in an arbitrary unit. In the present investigation the unit was so chosen that at the standard temperature of 18° C. the value of k becomes unity. By a special series of measurement, in which the concentration of the enzyme remained the same while the temperature was varied, the temperature coefficient of k was determined. It was found to be 1.21 for 10°, a surprising small value, which proves that the velocity of the reaction is mainly determined by that of diffusion.

The temperature coefficient of k′ was found to be somewhat larger, *i.e.*, 1.40. With these temperature coefficients and the value of k′ at 18° C. it is possible to describe the course of reaction at any temperature and for any initial values of the concentrations of the enzyme and the peroxide. The equation for the purpose has the form:

$$C = \frac{(kE_o - k'C_o)C_o}{kE_o e^{(kE_o - k'CO_o)t} - k'C_o} \quad ,(d)$$

or

$$C = \frac{C_o}{1 + k'C_o t} \qquad (e)$$

In the cases where $kE_o - k'C_o > o$, the reaction proceeds to the complete disappearance of hydrogen peroxide, while in the opposite cases where $kE_o - k'C_o < o$ the reaction does not proceed beyond a certain value of C. When $kE_o - k'C_o = o$ equation (e) describes the course of the reaction. These equations were found fully adequate to represent the experimental results.

ZUR SYSTEMATIK DER KOLLOIDE

Von Richard Zsigmondy

Im Jahre 1903, zu einer Zeit, wo die Eigenschaften kolloider Lösungen noch sehr unvollständig bekannt waren, hat Arthur Müller[1] eine Einteilung der Hydrolsole in 2 Klassen vorgeschlagen, die fundamental von einander verschieden sein sollten. Zu der einen rechnete er die Metalle und Sulfide, die er als Suspensionen feiner Teilchen ansah, die andere, zu der er Lösungen von Stoffen wie Gelatine aund Eiweiss zählte, sprach er als Lösungen hochmolekularer Verbindungen an. Die Geringfügigkeit des osmotischen Drucks bei den letzteren betrachtete er als Folge des hohen Molekulargewichts der in Betracht kommenden normal gelösten Stoffe.

Wir wissen heute, dass kolloide Metalle bis zur optischen Homogenität zerteilt werden können, sich dann in optischer Hinsicht vollkommen wie krystalloide Lösungen von Farbstoffen verhalten; dass Gelatinelösungen, viele Eiweiss—und Farbstofflösungen oft ganz erfüllt sind von sichtbaren Ultramikronen, dass man Gelatine—Eiweiss—und andere Kolloidlösungen durch Kollodiummembranen, *die für Krystalloide vollständig durchlässig sind*, abfiltrieren kann, wie kolloides Gold, dass also in Bezug auf räumliche Diskontinuität zwischen den als "Suspensionen" und den als Lösungen bezeichneten Systemen kein wesentlicher Unterschied besteht. Eine rein molekulare Zerteilung, wie sie *Muller* allgemein für die letzteren angenommen hat, erweist sich nur als Spezialfall, der in wenigen, seltenen Fällen realisiert erscheint (z. B. beim Rinderhämoglobin nach Hüfner[2]).

Die Elektrolytempfindlichkeit, die Müller als charakteristisches Merkmal für die suspensoide Natur der Metallkolloide und ähnlicher Systeme ansieht, erweist sich gleichfalls als unzureichend, um einen Unterschied zwischen Lösungen und Suspensionen herauszukonstruieren. Es genügt ja ein *minimaler* Zusatz von Schutzkolloid, der die Viskosität des Systems in keiner Weise erhöht, um eine Metallkolloidlösung ebenso elektrolytbeständig zu machen wie eine Eiweisslösung. Die Grösse der Metallteilchen wird durch diesen Zusatz nicht geändert, er genügt aber. um das Verhalten des Systems gänzlich zu ändern, die "suspensionsähnliche" Flussigkeit in eine "lösungsähnliche" zu verwandeln.

---

[1] *A. Müller*, Z. anorg. Chem. *36*, p. 340 (1903).

[2] G.Hüfner, Engelmanns Archiv. f. Physiol. Physiol. Abt. *1894*, p. 130; (*1904*) p. 217; *1907*, p. 209.

Die Theorie der Brown'schen Bewegung (Einstein[1]; v. Smoluchowski[2]) lässt voraussehen, dass auch den kolloiden Sulfiden, Metallkolloiden, etc., ein osmotischer Druck gegen ihr Filtrat zukommt, der, wenn störende Momente fehlen, der Teilchensahl proportional ist. Der Grund warum er sich meist der Messung entzieht, liegt in der Unmöglichkeit, die nur in grosser Verdünnung beständigen, *reinen*, schutzkolloidfreien Metallkolloide genügend weit zu konzentrieren. Bei As_2S_3—Solen haben Picton und Linder[3] tatsächlich osmotischen Druck nachgewiesen, Whitney und Blake[4] wie The Svedberg[5] konnten bei Gold Diffusion nachweisen[6].

Bei Kolloiden, die sich stärker konzentrieren lassen ohne dabei zu koagulieren, erreicht der osmotische Druck nicht nur messbare, sondern auch zuweilen ganz beträchtliche Höhen.

Also auch in bezug auf osmotische Eigenschaften ist ein prinzipieller Unterschied zwischen beiden Zerteilungsarten nicht zu machen.

Im Anschluss an A. Müller[7] und Bechhold[8] teilt Noyes[9] die Kolloide gleichfalls in 2 Gruppen, die "kolloiden Suspensionen" und die "kolloiden Lösungen", und kennzeichnet die ersten als nicht zäh, nicht gelatinierend und leicht durch Salze koagulierbar, die letzten als zähe, gelatinierend und durch Salze nicht koagulierbar. Statt des Ausdrucks "kolloide Suspensionen" sind zur Bezeichnung der oben charackterisierten Systeme noch mehrere

[1] A. Einstein, Annalen d. Phys. (4) *17*, p. 549 (1905); *19*, p. 371 (1906). Z.f. Elektrochem. *14*, p. 235 (1908).

[2] M.v. Smoluchowski, Annalen d. Phys. (4) *21*, p. 756 (1906); 25, p. 205 (1908).

[3] H. Picton und S. E. Linder, Journ. Chem. Soc. *61*, p. 114 (1892).

[4] Whitney und Blake, Journ. of the Amer. Chem. Soc. *26*, 1361, 1904.

[5] The Svedberg, Zeitschr. f. physikal. Chem. *67*, 105, 1909.

[6] Es kann kaum einem Zweifel unterliegen, dass die relativ hohe Konzentration, die Blake bei seinem Gold erzielte, auf Anwesenheit von Spuren von Schutzstoffen beruhte, welche die Teilchenvereinigung verhinderten.

[7] A. Müller, Z. anorg. Chem. *36*, p. 344 (1903).

[8] H. Bechhold, Z. phys. Chem. *48*, p. 393 (1904).

[9] Arthur A. Noyes, Journ. of Amer. Chem. Soc. *27*, p. 85 (1905).

andere vorgeschlagen worden: Hydrophobe Kolloide (Perrin), lyophobe Kolliode (Freundlich), Suspensionskolloide (Höber, Wo. Ostwald), Suspensoide (v. Weimarn) usw.; statt der Bezeichnung "kolloide Lösung" die Ausdrücke: Hydrophile, lyophile Kolloide, Emulsionskolloide, Emulsoide usw.

Es scheint bisher übersehen worden zu sein, dass eine Einteilung der Kolloide nach obigem Schema, da es viele Merkmale in Betracht zieht, underchführbar ist. Es gibt, z.B., "nicht zähe" und schwer durch Elektrolyte fällbare Kolloide, die in obiger Einteilung keinen Platz finden, so Paal's kolloides Silber. Kolloide Zinnsäure ist gelatinierbar, fällt aber leicht durch Elektrolyte, ist darum ebensowenig einer oder der anderen Klasse einzuordnen.

Einige der genannten Forscher haben die zahl der Merkmale noch vermehrt und damit die Einteilung nicht verbessert; durch die Ausdrücke "Suspensions"—und "Emulsionskolloide" werden Vorstellungen über den Aggregatzutand der zerteilten Materie fixiert, die keineswegs der Wirklichkeit zu entsprechen brauchen.

Für die folgenden Ausführungen ist noch auf eine Schwierigkeit hinzuweisen, die darin besteht, dass die Eigenschaften zäh, gelatinierbar und durch Elektrolyte leicht fällbar nicht eindeutig bestimmt sind. So hängt die Zähigkeit sehr von der Konzentration ab; Gallerten entstehen aus einem Sol zuweilen durch Temperaturänderung, zuweilen durch andere Einflüsse, und die Einteilung ändert sich je nachdem man unter "gelatinierbar" die Fähigkeit, Gallerten überhaupt zu bilden oder nur die Eigenschaft bei Temperaturerniedrigung zu gelatinieren versteht.

Die Elektrolytfällbarkeit endlich variiert in weitestem Masse je nach der Art der Elektrolyte, die in Betracht kommen. So braucht Albumin sehr viel Alkalisalz zu seiner Fällung, wird aber schon durch geringe Mengen Schwermetallsalze koaguliert.

In der folgenden Tabelle I können daher einige der angeführten Kolloide auch an eine andere Stelle gesetzt werden, falls man die Begriffe Gelatinierbar, etc., anders auffasst als ich. Durch geeignete Kombination der oben gegebenen Eigenschaften kann man zu folgenden 8 Klassen von Kolloiden kommen, und es ist nicht schwer, einen oder mehrere Repräsentanten für die Mehrzahl derselben zu finden.

TABELLE I

Klasse	*Eigenschaften*	*Beispiele*
1	Zäh, gelatinierbar, durch Elektrolyte schwer fällbar	Gelatine u. and.
2	Zäh, gelatinierbar, leicht fällbar	Graham's Caramel, Seifenlösungen, etc.
3	Zäh, nicht gelatinierbar, schwer fällbar	Dextrin, Grahams koll. Wolframsäure
4	Zäh, nicht gelatinierbar, leicht fällbar	
5	nicht zäh, gelatinierbar, schwer fällbar	Koll. Kieselsäure[1]
6	nicht zäh, gelatinierbar, leicht fällbar	Benzopurpurin[2], Graham's Koll. Tonerde.
7	nicht zäh nicht gelatinierbar, schwer fällbar	Paal's koll. Metalle
8	nicht zäh nicht gelatinierbar, leicht fällbar	Schutz kolloidfreie Metalle, einige Sulfide, etc.

Aus folgendem Schema[3] (Tabelle II) ergibt sich, dass die Einteilung von Noyes nur zwei sehr weit voneinander entfernte Gruppen von Kolloiden näher charakterisiert. Die Mehrzahl derselben ist keiner der beiden Klassen einzuordnen.

TABELLE II

Umfang der Klasse I			Umfang der Klasse II
Beispiele: Gelatine Stärke und einige andere "Colloidal solutions"	Dextrin Caramel Thoriumoxyd Aluminiumoxyd Kongorot, etc.	Cassius'scher Purpur Zinnsäure Seifenlösungen Einige Sulfide Benzopurpurin, etc.	Beispiele: Reine Metallkolloide, einige Sulfide und Salze, etc. "Colloidal suspensions"

Auch Wo. Ostwald[4] ist bei dem Versuche, die Einteilung in "Suspensions" und "Emulsionskolloide" (bezw. "Suspensoide" und "Emulsoide") praktisch durchzuführen, schliesslich zu dem Resultate gelangt, dass sie unzweckmässig, "zuweilen sogar unmöglich" ist. Er schreibt darüber unter anderem:

"Sodann sind die speziellen Abteilungen[5] "Suspensoide" und "Emulsoide" weggefallen zugunsten der Rubrik "Spezielle experimentelle Kolloidchemie" aus der praktischen Erkenntnis heraus, dass in auserordentlich viel Fällen sich die Unterschiede zwischen diesen zwei Klassen Kolloider Lösungen verwischen."

---

[1] Kieselsäure zeigt nur vor dem Gelatinieren eine beträchtliche (Zähigkeitszunahme).

[2] Gelatinierbar, zum Beispiel, bei der Dialyse.

[3] Das Schema und die Stellung der Beispiele in Tabelle I ändern sich etwas, wenn man die wörter zäh, gelatinierbar etc., anders auffasst als ich, aber immer werden sich zahlreiche Repräsentanten von Hydrosolen finden, welche in keiner der beiden Klassen von Noyes-Platz haben.

[4] *Wo. Ostwald*, Koll. Z. 9. p. 29 (1911).

[5] In der Literaturübersicht der Kolloid-Zeitschrift (Anmerkung der Referenten. Z.)

Die Wo. Ostwald'sche Einteilung nach dem Aggregatzustande der zerteilten Materie würde brauchbar sein, wenn man ein Mittel hätte, den Aggregatzustand (Formart) der Ultramikronen festzustellen. Dies ist aber in weitaus den meisten Fällen unmöglich. Ausserdem zeight das Beispiel des kolloiden Quecksilbers,[1] dass das Verhalten der Hydrosole durch den Aggregatzustand der zerteilten Materie nicht wesentlich bestimmt wird, dass jedenfalls andere Faktoren als bloss der Aggregatzustand der zerteilten Materie dafür massgebend sind, ob ein gegebenes Kolloid sich wie ein lyophiles oder wie ein lyophobes verhält. Nach neueren Ausführungen von Wo. Ostwald[2] soll es hauptsächlich auf den komplexen Charakter des "Dispersoids" ankommen und der Aggregatzustand der dispersen Phase soll bei "Emulsoiden stetig variieren können zwischen vollkommen flüssig über zähflüssig zu fest, damit verlieren aber die Einteilung nach dem Aggregatzustand und ebenso die Wörter Suspensions—und Emulsionskolloide ihre Bedeutung.

Im folgenden will ich nun eine Einteilung besprechen, die jedenfalls den Vorzug hat bezüglich der bei gewöhnlicher Temperatur und Atmosphärendruck beständigen Kolloidlösungen[3] durchfuhrbar zu sein. Sie ist schon vor mehreren Jahren vorgeschlagen worden[4].

Man kann die Kolloide je nach ihrem Verhalten beim Eintrocknen in 2 Klassen einteilen. Zur ersten Klasse gehören kolloide, die einen Trockenrückstand hinterlassen, der im Dispersionsmittel wieder selbständig zum ursprunglichen Sol zerteilbar ist, zur zweiten Kolloide, denen diese Eigenschaft abgeht. Kolloide der ersten Klasse, zu denen Dextrin, Gummi arabicum, Eiweiss,

---

[1] Physikalische Zeitschr. XI. p. 654 (1910).

[2] *Wo. Ostwald*, Grundriss der Kolloidchemie, 2 Aufl, p. 61 (1911).

[3] Es sind das wohl alle wichtigen Kolloidlösungen. Auf disperse Systeme, die nur bei sehr hohen orde sehr niedrigen Temperaturen oder bei extremen Drucken beständig sind, soll hier nicht eingegangen werden. Sie nehmen schon auf Grund ihrer Beständigkeitsbedingungen eine besondere Stellung ein und können auf Grund dieser in einer künftigen Einteilung den ihnezukommenden Platz angewiesen bekommen. Auch sind vorwiegend Hydrosole in Betracht gezogen, obgleich die Einteilung auch auf Organosole Anwendung finden kann.

[4] R. Zsigmondy, Zur Erkenntnis der Kolloide, Jena, 1905, Kap. II.

Gelatine, etc., gehören, wurden mit einem von Hardy[1] allerdings in anderem Sinne gebrauchten Ausdruck "*reversible* Kolloide" bezeichnet, Kolloide der zweiten Klasse mit dem Ausdruck *irreversible* Kolloide.

Um jedes Missverständnis auszuschliessen, dass es sich hier um die ursprüngliche Hardy'sche Einteilung handelt, deren Undurchführbarkeit schon früher nachgewiesen worden war,[2] sehe ich mich, trotzdem ich kein Freund der modernen Ueberschwemmung der Kolloidchemie mit neuen Wörtern bin, genötigt doch einen neuen Ausdruck einzuführen. Systeme der ersten Klasse seien daher als *resoluble* Kolloide, die der zweiten Klasse als *irresoluble* bezeichnet.

Die Durchführbarkeit dieser Einteilung ist ohne weiteres ersichtlich; man braucht nur das Kolloid bei Zimmertemperatur zur Trockne einzudampfen und zu prüfen, ob bei Berührung mit dem Dispersionsmittel das Sol mit seinen ursprünglichen Eigemschaften zurückgewonnen werden kann oder nicht.

Bei einigen der Kolloide ist dabei Temperaturerhöhung erforderlich, bei anderen nicht. Das gibt Veranlassung zu einer weiteren Einteilung:

Zur einen Gruppe der resolublen (reversiblen) Kolloide gehören Gelatine, Agar, Stärke, etc., zur anderen Dextrin, Gummi arab., Albumin, Graham's Molybdän und Wolframsäure, Lea's Silber, Paal's Gold.

Auch die irresolublen (irreversiblen) Kolloide lassen sich weiter einteilen:

Eine Gruppe von ihnen enthält Systeme, die schon während des Konzentrierens der kolloiden Lösung koagulieren und zwar so weitgehend, dass eine Peptisation des (meist pulvrigen) Niederschlags nicht mehr möglich ist, d.h. dass sie sich durch Hinzufügen kleiner Mengen von geeigneten Krystalloiden (Säuren, Alkalien, Salze) nicht mehr in das ursprüngliche Hydrosol zurückverwandeln lassen. Hierher gehören die schutzkolloidfreien kolloiden Metalle.

Die zweite Gruppe umfasst Kolloide, die sich weitgehend konzentrieren lassen, um bei erheblicher Konzentration zu koagulieren, wobei peptisierbare Gallerten entstehen (Zinnsäure, Kieselsäure, Eisenoxyd und Graham's Tonerde, etc.). Erst bei vollständigem Eintrocknen verliert sich meits die Peptisierbarkeit.

---

[1] W. B. Hardy, Z. phys. Chem. *33*, p. 326-385 (1900).

[2] R. Zsigmondy, Zur Erk.d. Koll. p. 20.

Als Typus der ersten Gruppe kann das kolloide Gold, als Typus der zweiten die kolloide Zinnsäure angesehen werden.

Die kolloiden Sulfide stehen ungefähr in der Mitte zwischen diesen beiden Typen von Kolloiden, d.h. sie lassen sich je nach der Peptisierbarkeit des schon während des Eindampfens entstehenden Koagulums der einen oder der anderen Gruppe einordnen.

Das einfache Eindampfen und Wiederauflösen gibt demnach eine Reihe von Anhaltspunkten über die Natur des Kolloids und ermöglicht eine Einteilung in Gruppen, deren Glieder eine Anzahl charakteristischer Merkmale miteinander gemein haben. Die Einteilung ist unaghängig vom Dispersitätsgrad, d.h. in jeder einzelnen Gruppe können Glieder enthalten sein, die sowohl relativ grobe wie nahezu optisch homogene Zerteilungen enthalten.

Man könnte dieser Einteilung zum Vorwurf machen, dass sie die Temperatur des Eintrocknens und Wiederauflösens willkürlich auf Zimmertemperatur (15°-20° C.) festsetzt. Dieses Temperaturintervall ist aber das natürliche, durch unsere Arbeitsbedingungen von selbst gegebene: bei Zimmertemperatur operieren wir mit den Kolloidlösungen, bei Zimmertemperatur werden sie aufbewahrt, und wir sind fast immer genötigt, unsere Substanzen, wenn wir sie bei anderen Temperaturen beobachten wollen, einer künstlichen Temperatursteigerung oder—Erniedrigung auszusetzen.

Die Tabelle III gibt eine Uebersicht über die Einteilung.

TABLE III

EINTEILUNG NACH DEM VERHALTEN BEIM EINTROCKNEN

I. Resoluble Kolloide

(Die Kolloide lösen sich selbständig im Dispersionsmittel)

A. Zur Herstellung der kolloiden Lösung der bei Zimmertemperatur eingetrockneten Kolloide ist Temperaturerhöhung erforderlich[1]: Gelatine, Stärke, Agar-Agar, viele Seifen, etc.

B. Zur Herstellung der kolloiden Lösung ist *keine* Temperaturerhöhung erforderlich: Dextrin, Gummi arab., Paal's koll.

---

[1] Der Zerteilungsgrad ist in auffälliger Weise von der Temperatur abhängig.

Metalle, überhaupt geschützte Metallkolloide, Graham's Wolfram und Molybdänsäure, Molybdänblau, Albumin, etc.

II. Irresoluble Kolloide

(Die Kolloide lassen einen unlöslichen Trockenrückstand zurück, da sie beim Eintrocknen irreversible Zustandsänderungen erleiden (darum auch *irreversible* Kolloide gennant).

A. Kolloide, die pulvrige, nicht mehr peptisierbare Niederschälge schon während des Eintrocknens geben: Reine Metallkolloide, einige Sulfide, Salze wie AgBr, AgCl, etc.

B. Kolloide, die beim Eintrocknen irreversible Zustandsanderungen erleiden und zunächst peptisierbare Gallerten geben: Zinnsäure, Kieselsäure, Eisenoxyd, Tonerde (Graham's).

Zur praktischen Durchführung dieser Einteilung muss allerdings das noch wenig bekannte Verhalten der einzelnen Kolloidlösungen beim Eintrocknen näher studiert werden. Auch macht sie erforderlich, dass Hydrosole, die gegenwärtig noch mit dem gleichen Namen bezeichnet werden, von einander getrennt werden. Ich habe daher in mienem Buche[1] "Kolloidchemie" die folgende Einteilung der Kolloidsysteme durchgeführt, die jedenfalls zünachst eine leichtere Orientierung gestattet als die oben näher erörterte:

I. Anorganische Kolloide

- A. Metalle:
  - 1. Reine Metallkolloide
  - 2. Metallkolloide mit Schutzkolloiden
- B. Andere Elemente (S, Se, etc.)
- C. Oxyde
- D. Sulfide
- E. Salze

II. Organische Kolloide

- A. Organische Salze:
  - 1. Seifen
  - 2. Farbstoffe
- B. Eiweisskörper:

Daran können andere Kolloide Z. B. Kohlehydrate angeschlossen werden.

---

[1] R. Zsigmondy, Kolloidchemie, Leipzig, 1912, Verl. Spamer.

Noch seien einige Werte über ein viel weiteres Gebiet, das der dispersen Systeme, dem die Kolloidlösungen selbst eingeordnet werden können, eingefügt. Will man die Gesamtheit der Zerteilungen (disperse Systeme) einteilen, so wird man sich mit grossem Vorteil an die Wo. Ostwald'sche Einteilung halten und die dispersen Systeme zunächst nach dem Aggregatzustand (Format) des Dispersionsmittels scheiden:

I. Disperse Systeme mit gasförmigem Dispersionmittel: Nebel (G+Fl), kosmischer Staub (G+F), etc.

II. Disperse Systeme mit flüssigem Dispersionsmittel: Gröbere Systeme: Suspensionen (Fl+F). Emulsionen (Fl+Fl): Feinere Systeme: hierher gehören die kolloiden Lösungen als feinere Zerteilungen ursprünglich fester Körper in Flüssigkeiten.

Ich halte es nicht für zweckmässig, diese selbst nach dem Aggregatzustand der zerteilten Materie (der meist unbekannt ist) einzuteilen[1], sondern zunächst nach den Bestandigkeitsbedingungen der dispersen Systeme: Solche die nur bei hoher Temperatur als flüssige Systeme beständig sind, Pyrosole (R. Lorenz): solche die bei gewöhnlicher Temperatur beständig sind, Sole Graham's oder kolloide Lösungen im engeren Sinne: solche, die nur bei tiefen Temperaturen beständig sind, einige Metallsole nach Svedberg, kolloides Eis (Wo. Ostwald, v. Weimarn), Kryosole.

Die weitere Einteilung erfolgt dann zweckmässig nach der Natur des Dispersionsmittels, also mit Graham in Hydrosole, Sulfosole, Alkosole, Aetherosole, etc. Diese letzteren könnten weiter nach ihrem Verhalten beim Eintrocknen in der oben geschilderten Weise klassifiziert werden.

Eine Fortführung der Einteilung könnte erzielt werden, wenn man die Natur der zerteilten Materie in Betracht zeiht (in Elemente, Oxyde, Sulfide, etc., organische Kolloide), oder, indem man die Sole in elektrolytähnliche und nichtelektrolytähnliche einteilte, oder endlich, indem man das Verhlten gegen einzelne *ganz bestimmte* Elektrolyte untersuchte und nach diesem enteilte (eine Klassifikation, ähnlich der in der analytischen Chemie üblichen).

---

[1] Diese Einteilung würde eine Unzahl von Spezial Hypothesen bezüglich des Aggregatzustandes (Format) der dispersen Phase erforderlich machen und Streitfragen über den Aggregatzustand heraufbeschwören.

III. Disperse Systeme mit *festem* Dispersionsmittel könnten eingeteilt werden zunächst etwa in Systeme mit krystallisiertem und mit amorphem Dispersionsmittel.

Die modificierte Ostwald'sche Einteilung der dispersen Systeme würde sich ungefähr folgendermassen gestalten (Tabelle IV).

TABELLE IV

EINTEILUNG DER DISPERSEN SYSTEME

I. Disperse Systeme mit gasformigem Dispersionsmittel

A. Grob disperse Systeme:

(a) G+Fl: Regen, Nebel

(b) G+F: vulkanischer Aschenregen, vulkanischer Staub in der Atmosphäre, nuée ardente.

B. Fein disperse Systeme:

Atmosphäre mit kleinen Teilchen, die nach Lord Rayleigh am Zustandekommen des Himmelsblau beteiligt sind; Metallzerstäubungen (Ehrenhaft).

II. Disperse Systeme mit flüssigem Dispersionsmittel

A. Grob disperse Systeme: Teilchengrösse bis zu 0,1 u herab

(a) Fl+F: Suspensionen:

(b) Fl+Fl: Emulsionen.

B. Fein disperse: Systeme: Teilchengrösse zwischen etwa 0,1 und 0,001 u—

(a) Pyrosole: Metallnebel in geschmolzenen Salzen

(b) Kolloide Lösungen im engeren Sinne

mit anorganischem Dispersionsmittel:

1. Hydrosole
   1. Resoluble Hyrdosole vom Dextrintypus—vom Gelatinetypus
   2. Irresoluble Hydrosole vom Typus der Zinnsäure—vom Typus des Goldes
2. Sulfosole u. andere.

mit organischem Dispersionsmittel (Organosole)

z.B. Alkosole, Aethersole, Acetosole, etc.

c)Kryosole: Einige Koll. Metalle (Svedberg), koll. Eis (v. Weimarn, Wo. Ostwald).

III. Disperse Systeme mit festem Dispersionsmittel

- A. Grob disperse Systeme:
  - (a) F+F: Gesteinsarten (erstarrte Pyrosole, Silikate):
  - (b) F+Fl: Mineralien mit flüssigen Einschlüssen:
  - (c) F+G: Mineralien mit gasförmigen Einschlüssen.
- B. Fein disperse Systeme:
  - (a) Zerteilungen in krystallisierten Substanzen (Gefärbtes Steinsalz, Rubine, Mondstein, etc.)
  - (b) Zerteilungen in amorphen Substanzen (Rubingläser, Opale, etc.)

Die Einteilung könnte noch beträchtliche Erweiterung erfahren, wenn man die Klassen I und III, nach Beständigkeitsbedingungen etc., einteilte, ähnlich wie Klasse II. Vorläufig ist eine solche Erweiterung nicht erforderlich.

In voliegender Abhandlung musste ich mich aus sachlichen Gründen gegen die Einteilung von Noyes aussprechen. Meine Einwände richten sich aber nicht gegen die sonstigen Ausführungen dieses Forschers, der den Gegenstand im übrigen in vorzüglicher Weise und mit grossem Scharfsinn beurteilt hat. Vor allem sollen die ausgeseichten Worte, die Noyes im Anschluss an die Besprechung der Koagulation bezüglich einer modernen Richtung in der Kolloidliteratur zum Ausdruck brachte, hier wiederholt werden. Seine Worte verdienten nicht nur so oft wie möglich abgedruckt zu werden, sie sollten in alle Sprachen übersetzt werden.

Noyes[1] schreibt bezüglich der Erklärungsversuche betreffs des Mechanismus der Koagulation:

"Interesting though they are, I shall not try to describe the explanations that have been suggested, for, in my opinion, mere speculative hypotheses, that is, hypotheses which have not been shown to facilitate to an important extent a knowledge of the actual phenomena, are of little value except to the investigators of them and to them only because of the possibility of their future development into really useful conceptions. The recent

---

[1] Arthur A. Noyes, Journ. of Amer. Chem. Soc. *27*, p. 103 (1905).
Göttingen, Institut für anorganische Chemie.

literature of colloids furnishes a striking example of the unfortunate tendency even of our modern investigators and text-book writers to attach greater importance to hypothetical interpretations of imperfectly known phenomena than to a determination and presentation of the laws in regard to them."

GENERAL INDEX
TO THE TWENTY-FOUR VOLUMES OF ORIGINAL COMMUNICATIONS

Volume		Section
1	I.	Analytical Chemistry.
2	II	Inorganic Chemistry.
3	IIIa	Metallurgy and Mining.
4	IIIb	Explosives.
5	IIIc	Silicate Industries.
6	IV	Organic Chemistry.
7	IVa	Coal Tar Colors and Dyestuffs.
8	Va	Industry and Chemistry of Sugar.
9	Vb	India Rubber and other Plastics.
10	Vc	Fuels and Asphalt.
11	Vd	Fats, Fatty Oils and Soaps.
12	Ve	Paints, Drying Oils and Varnishes.
13	VIa	Starch, Cellulose and Paper.
14	VIb	Fermentation.
15	VII	Agricultural Chemistry.
16	VIIIa	Hygiene.
17	VIIIb	Pharmaceutical Chemistry.
18	VIIIc	Bromatology.
19	VIIId	Biochemistry including Pharmacology.
20	IX	Photochemistry.
21	Xa	Electrochemistry.
22	Xb	Physical Chemistry.
23	XIa	Law and Legislation Affecting Chemical Industry.
24	XIb	Political Economy and Conservation of Natural Resources.

ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS
OF APPLIED CHEMISTRY

Washington and New York

September 4 to 13, 1912

SECTION XI*a*.—LAW AND LEGISLATION AFFECTING CHEMICAL INDUSTRY

VOL. XXIII

ORIGINAL COMMUNICATIONS
EIGHTH INTERNATIONAL
CONGRESS OF APPLIED CHEMISTRY

Washington and New York
September 4 to 13, 1912

SECTION XI*a*.—LAW AND LEGISLATION AFFECTING CHEMICAL INDUSTRY

VOL. XXIII

The matter contained in this volume is printed in exact accordance with the manuscript submitted, as provided for in the rules governing papers and publications.

La matière de ce volume a été imprimée strictement d'accord avec le manuscrit fourni et les règles gouvernant tous les documents et publications.

Die in diesem Heft enthaltenen Beiträge sind genau in Übereinstimmung mit den uns unterbreiteten Manuskripten gedruckt, in Gemässheit der für Beiträge und Verlagsartikel geltenden Bestimmungen.

La materia di questo volume e stampata in accordo al manoscritto presentato ed in base alle regole que governano i documenti e le publicazioni.

THE RUMFORD PRESS
CONCORD·N·H·U·S·A·

ORIGINAL COMMUNICATIONS

TO THE

EIGHTH INTERNATIONAL CONGRESS

OF

APPLIED CHEMISTRY

APPROVED

BY THE

COMMITTEE ON PAPERS AND PUBLICATIONS

IRVING W. FAY, CHAIRMAN

T. LYNTON BRIGGS
F. W. FRERICHS
A. C. LANGMUIR
JOHN C. OLSEN
JOSEPH W. RICHARDS
E. F. ROEBER
A. F. SEEKER

SECTION XI*a*.—LAW AND LEGISLATION AFFECTING CHEMICAL INDUSTRY

Executive Committee

President: The Honorable Edward D. White, Chief Justice of the Supreme Court of the United States
Vice-President: William L. Dudley, B.S., M.D.
Secretary: John C. Pennie
Frederick P. Fish, A.B.
Alfred Springer, Ph.D.

Sectional Committee

Charles Alling, Jr., LL.B., M.A.
Ivan M. Bregowsky
Arthur von Briesen
Orville S. Brumback
J. Edgar Bull
Eugene A. Byrnes, Ph.D.
James L. Gerry
Livingston Gifford
Edward Gudeman, Ph.D.
James I. Kay
Thomas B. Kerr
A. D. Little
Harry McCormack, M.S.
K. P. McElroy
Howard S. Neiman, A.C., B.S.
Robert H. Parkinson
James H. Peirce, B.S., LL.B.
A. L. J. Queneau
George W. Rea, LL.B.
Charles L. Reese, Ph.D.
Joseph W. Richards, Ph.D.
Clifford Richardson, F.C.S.
Jokichi Takamine, Dr. Ing., Phar.D.
Charles C. Trabue, B.A., LL.B.
Frank S. Washburn, C. E.

and the Sectional Executive Committee

VOLUME 23

SECTION XI*a*.—LAW AND LEGISLATION AFFECTING CHEMICAL INDUSTRY

CONTENTS

Aeby, Dr. Julius.
The Transportation of Dangerous Goods by Water 7

Allart, Andre.
Dénominations des Produits Pharmaceutiques 13

Allart, Andre.
Législation Internationale sur l'Importation des Produits Revêtus d'une Marque de Commerce 19

Husson, A.
Nécessité d'Activer la Solution des Procés Concernant la Propriété Industrielle 25

Jacq, Fernand.
La Fabrication dans un Pays de la Convention Internationale de la Propriété Industrielle Protege le Possesseur d'un Brevet Dans Toutes les Nations Faisant Partie de la Convention 31

Jacq, Fernand.
Législation Internationale Uniforme pour les Brevets et les Marques 35

Jacq, Fernand.
Les Brevets Internationaux Sont-Ils Desirables ou Non? 39

Jacq, Fernand.
Mise en Oeuvre Obligatoire des Inventions et Licence Obligatoire 47

Laire, Ed. de
Brevet International Permettant de Simplifier les Contestations Entre Etrangers 55

Laire, Ed. de
Examen Préalable des Brevets 61

McDermott, Edward J.
Expert Testimony 67

Taillefer, A.
De la Brevetabilite des Produits Pharmaceutiques 79

Taillefer, Andre.
De l'Utilite d'un Enregistrement International de Plis Cachetes 83

THE TRANSPORTATION OF DANGEROUS GOODS BY WATER

BY DR. JULIUS AEBY
Antwerp, Belgium

In the two preceding Congresses, at Rome in 1906 and London in 1909, the question of the transportation of dangerous goods by water has already been treated by Dr. C. A. von Martius of Berlin. I therefore deem it unnecessary to particularly insist on the reasons in favor of the solution of a problem equally interesting to chemical factories, navigation companies, underwriters and, last but not least, the passengers and crews of steamers and sailing ships. It will be sufficient to study the two mentioned reports,[1] but what I wish first of all to point out is that, as far as I know, Dr. von Martius' appeal for an international regulation of the question, and the summoning of a conference to this effect, has not obtained even the commencement of a solution, whilst, on the other hand, the number of accidents increases, and the difficulties between manufacturers and shippers are augmenting. This is forcibly brought to my notice in the course of a regular practice with the shipping companies in Antwerp.

To fully comprehend the question, it will be necessary, first of all, to briefly enumerate the principal authors who have occupied themselves with it, and the publications relating to same.

In chronological order:

1. "*Die Selbstentzündung von Schiffsladungen, Baumwolle und anderen Faserstoffen, Steinkohlen, Heuhaufen, Tabak, etc., sowie deren Verhütung.*"
   "The spontaneous combustion of cargos, cotton and other fibrous material, coal, haystacks, tobacco, etc., and the means

---

[1] (1) Report of the Sixth International Congress of Applied Chemistry at Rome, 1906, "International Regulation of prescriptions on the transport by post, railway and sea, of explosive, easily combustible, corrosive, etc., products."
(2) Report of the Seventh International Congress of Applied Chemistry at London, 1909, "On the Transportation of Dangerous Goods by Merchant Ships."

of prevention." By Dr. L. Häpke. (Bremen, Publisher, C. Ed. Müller, 1893.)

2. "*The Handling of Dangerous Goods.*"
   By H. Joshua Philips. (London, Crosby Lockwood and Son, 1896.)
3. *Abgeänderte Unfallverhütungsvorschriften der Seeberufsgenossenschaft für Dampfer.*
   "Modified prescriptions for the prevention of accidents, laid down by the Professional Marine Association for steamers." (Hamburg, H. O. Persiehl, 1903.)
4. *Memorandum relating to the carriage of dangerous goods and explosives in ships.*
   Board of Trade. (London, Wyman and Sons, 1907.)
5. *Reports of the Bureau for the safe transportation of explosives and other dangerous articles.*
   (New York, 1908-1909-1910-1911 and 1912.)
6. *Eisenbahn Verkehrsordnung.*
   "Rules for carriage by railway." (Berlin, Julius Springer, 1909.)
7. *Marchandises Dangereuses.*
   "Dangerous Goods." By Dr. Julius Aeby, (Antwerp, 1910.)
8. "*Polizei-Verordnung betroffend die Beförderung gefährlicher Gegenstände mit Kauffahrteischiffen.*"
   "Police rules, concerning the transport of dangerous goods by merchant ships." (Berlin, 1912.)

Finally, I must say that in the "Repertorium" of the "Chemiker Zeitung," chapter "Hygiene-prevention of Accidents," records are sometimes given of damage occurring in the transportation of dangerous goods.

All these studies are certainly very interesting and useful, but they do not give entire satisfaction to the shippers, for the following reasons:

(1) They are only published in one language.

(2) They are not complete, and, in some cases, lack a convenient index.

(3) They do not indicate in a sufficiently clear and concise manner those properties of goods with which shippers ought to be familiar.

In my book "Dangerous Goods" (quoted under N°7) published in 1910, I have endeavored to comply with the above-mentioned points, and the fact that it is now used regularly by many shipping companies in Europe, may be counted as a proof of its utility to this side of the interested parties. From the other side, *i.e.*, the chemical industry, I have been sharply criticized on this work by certain German parties (Chemische Industrie, 1911, pp. 146-238 and 605) and this appears to me an additional reason for urging that the representatives of the chemical industry of all countries here present should not underestimate the importance of this question.

As a result of the last annual meeting at Stuttgart, in 1911, of the "Union for the protection of the interests of the chemical industry in Germany," a commission was appointed of three members in order to study the question of the transportation of dangerous objects. This is a beginning, and with confidence we may await the results. But in the great country whose hospitality we are at present enjoying, there exists a perfected institution, too little known in Europe, and to which I wish to draw attention; I mean the "Bureau for the safe transportation of explosives and other dangerous articles" at Washington.

Great benefit would be derived from a study of the organization and the publications of this Bureau.

I have mentioned at the beginning of this report that the importance of the question of the transportation of dangerous merchandise can no longer be ignored. If I cite a few examples hereafter, it is only because nothing else would more forcibly justify the conclusions and resolutions which I desire to put before this Congress.

1. *Bleaching Powder.* Cases of decomposition accompanied by elevation of temperature have been observed, and fires on board of ships attributed to them. Bleaching powder, according to information from manufacturers, is capable of decomposition when freshly prepared, but, they say, only for three days after fabrication. Under these circumstances it will easily be understood that bleaching powder cannot be classified among the absolutely safe products, and it is only just to demand that the manufacturers should take necessary measures to avoid accidents.

2. *Permanganate of Potassium.* This compound was considered absolutely dangerless until the occurring of the following case: some of this salt, escaping from the packing, and mixing with dust of a combustible nature, caused the beginning of a fire under the influence of friction. In this respect, permanganate of potassium resembles peroxide of barium. The natural conclusion to be drawn from this fact is that the packing of this product should be very carefully supervised.

3. *Arsenic Acid.* This is a liquid regularly transported in iron drums to America, and one could hardly have foreseen the accident which happened at New York about a year ago. The explanation was found in the fact that the arsenic acid in question still contained traces of nitric acid. The latter burst the iron drums, and the contents sprayed over the men, causing the death of one of them. It will be necessary in future, therefore, to ensure that the arsenic acid does not contain an excess of nitric acid, and that it should be preserved against heat and the rays of the sun.

4. *Metallic Sodium.* In contact with water, this product is inflammable, and it is therefore quite evident that it should never be loaded on deck. The ignoring of this fact has, this year, caused the loss of a vessel, and the death of two of the crew.

5. *Cyanamide of Calcium.* Three years ago I already called attention to the danger of this manure, because, when badly manufactured, it still contains carbide of calcium, which, by the moisture in the air, gives off acetylene. My previsions have recently (in May last) received a sad confirmation in the blowing up of a Norwegian steamer loaded with cyanamide of calcium. Eight men were killed in this catastrophe, which would have been prevented if it had been known that the approach of a naked flame had to be strictly avoided.

It is useless to prolong the list of these examples. They prove sufficiently, I think, that no one, more so than the manufacturer himself, should indicate the necessary precautions to be taken in the transportation of certain goods. If the manufacturers do not themselves consider this question in an efficacious manner, it is probable that the shipping companies will have to take measures, or else the authorities whose duty it is to safeguard the public security. In the interest of all, I therefore propose the following resolutions:

1. It is desirable that this Congress should appoint an international commission of representatives of the chemical industry, in order to establish, and keep up to date, a list of dangerous goods; to centralize all communications on this subject; to study the special literature; to collect and examine samples; and, perhaps, organize an information service for governments, shipping companies, insurance companies, etc.

2. It is further desirable that this commission should invite to join them authorized representatives of shipping companies.

DENOMINATIONS DES PRODUITS PHARMACEUTIQUES

PAR ANDRE ALLART
Docteur en Droit. Avocat à la Cour de Paris

I

L'association médicale américaine a adressé dans le courant de mars 1912 aux fabricants et marchands de produits pharmaceutiques une circulaire dans laquelle elle propose l'établissement, pour la désignation des remèdes et médicaments, des règles suivantes:

I° Les noms des préparations pharmaceutiques devront indiquer les éléments les plus actifs entrant dans leur composition.

2° Les noms susceptibles de créer une confusion sur la nature du produit ne seront pas reçus comme marques.

3° Les noms qui suggèrent l'idée d'une maladie ou d'une vertu thérapeutique ne seront pas reçus comme marques.

C'est une réglementation nouvelle de la matière des marques qui se trouve proposée dans ces quelques articles. Elle se trouve même, par certains points, en antinomie complète avec les principes le plus communément admis sur ce sujet, et aboutit à créer dans le régime des marques de fabrique une division radicale entre les marques apposées sur des produits thérapeutiques et celles destinées aux autres objets du commerce.

En effet le principe fondamental et qui se retrouve dans la plupart des législations, est que la marque, pour faire l'objet d'un droit de propriété exclusive, doit être arbitraire et de fantaisie. Si elle est descriptive et indique la nature et l'objet du produit qu'elle recouvre, elle n'est plus protégée. Enfin, si elle est déceptive, c'est à dire si elle suggére l'idée d'une qualité du produit qui n'existe pas dans la réalité, elle peut être déclarée illicite.

Les propositions de l'Association médicale bannissent en quelque sorte la marque de fantaisie et la marque déceptive et la rendent obligatoirement descriptive.

Elles limitent même d'une façon étroite l'usage de cette dernière.

II

La première proposition exige que la marque indique les éléments les plus actifs entrant dans la composition du produit. C'est la marque descriptive rendue obligatoire. Elle est de nature à engendrer bon nombre de difficultés, sans utilité correspondante bien nettement établie.

Tout d'abord, pour un produit complexe, elle rend nécessaire une marque complexe difficile à retenir pour le public.

Elle crée entre toutes les marques relatives à un même produit, une similitude d'où peuvent résulter nombre de confusions. On propose, pour y remédier, l'adjonction d'une désinence de fantaisie ou d'un nom patronymique. Mais l'expérience montre que de telles adjonctions ne sont pas toujours suffisantes pour prévenir les confusions. L'acheteur placé devant une dénomination compliquée qui ne se différencie des autres dénominations appliquées au même produit que par l'adjonction d'une syllabe ,ou d'un nom, ou par une simple modification d'orthographe, ne sera pas toujours frappé par cette différence de façon suffisante pour les distinguer avec certitude.

Au contraire, la marque de pure fantaisie peut être concise et caractéristique, frapper l'esprit et s'imposer à la mémoire. Par là toute chance d'erreur est évitée. C'est pour cela que la dénomination arbitraire est devenue, dans la pratique, la marque par excellence. La supprimer est fort dangereux.

Comme contrepartie à ce danger, aucun avantage bien précis n'apparait.

L'indication de la composition du produit ne sera souvent que très insuffisante pour éclairer l'acheteur. Il faudrait que cette indication fût absolument complète et rappelât tous les éléments composants du produit, ce qui en fait, est impossible. Il faudrait, en outre, préciser les proportions dans lesquelles ils se trouvent dans le produit. Autrement on ne donne au public qu'une sécurité trompeuse: il croit connaitre la composition du produit qu'il acquiert, et dans la réalité il n'a qu'une indication insuffisante, propre à la tromper.

Ne vaut-il pas mieux ne pas le renseigner du tout que de le renseigner de cette façon? S'il sait que la marque qu'on lui offre, ne signifie rien, quant à la composition du produit, il ne sera pas amené à y attacher d'autre valeur qu'une valeur de référence, ce qui est, d'ailleurs, conforme à son objet.

La marque ne doit être qu'une indication d'origine; c'est une chose dangereuse que de la faire sortir de son objet pour en faire une indication de la composition et de la nature du produit qu'elle recouvre. Cela ne peut qu'engendrer l'erreur et la confusion.

III

La seconde proposition prohibe les marques déceptives pour les produits pharmaceutiques.

Pendant longtemps on ne s'est guère préoccupé des marques de cette nature. Il semblait au contraire qu'elles réalisaient un maximum de fantaisie et qu'il n'y avait aucune raison de révoquer en doute leur validité. Mais un revirement s'est produit dans la plupart des législations. On a voulu poursuivre et détruire la fraude en quelque manière qu'elle se produisît. On a ambitionné d'assurer à l'acheteur une sécurité complète en le prémunissant contre toute possibilité d'erreur. Les lois sur les fraudes sont devenues de plus en plus strictes et rigoureuses.

Dans cette voie, l'attention devait nécessairement se porter sur les marques qui paraissent indiquer la nature du produit qu'elles recouvrent, mais qui se réfèrent à des qualités qui ne lui appartiennent pas dans la réalité. Devait-on en interdire l'usage, comme étante de nature à tromper l'acheteur sur les qualités de la marchandise qui lui était offerte? C'est ce à quoi on s'est peu à peu acheminé, et nous ne pensons pas qu'il y ait lieu de le regretter.

Pour se rendre compte de l'évolution accomplie sur ce point, il faudrait suivre dans la jurisprudence de chaque pays, la façon dont ce genre de fraude a été de plus en plus rigoureusement réprimé par une application plus stricte des lois existantes. Il faudrait suivre le mouvement législatif lui-même, constamment plus sévère à cet endroit.

Il suffit de constater la généralité de cette tendance, pour se convaincre que la proposition que nous examinons n'en est qu'une étape particulière. Elle concorde avec un mouvement indiscutable qui s'accuse dans toutes les législations. Son adoption ne saurait à nos yeux soulever de sérieuse critique. Il restera toujours un nombre suffisant de dénominations de pure fantaisie pour que les commerçants ne soient pas en peine d'en trouver pour en faire leur marque de fabrique.

IV

La troisième proposition tend à refuser l'acceptation, comme marques, des noms suggérant l'idée d'une destination possible du produit. Elle a pour but d'éviter que le public croyant trouver, dans la dénomination apposée sur le produit, l'indication de ses vertus thérapeutiques ou des maladies auxquelles il peut servir de remède, ne se croie, par là, suffisamment éclairé pour en faire usage, sans se renseigner plus amplement sur l'opportunité de son utilisation.

Est-ce là une crainte bien fondée N'est-ce pas prêter à l'acheteur une légèreté bien grande que de supposer que, sur le vu d'une dénomination équivoque, il pourra être conduit à se faire son propre médecin?

D'un autre côté, cette disposition ne serait-elle pas en contradiction avec cette autre proposition selon laquelle la dénomination doit indiquer les éléments les plus actifs entrant dans la composition du produit? Une semblable indication, s'il est vrai qu'il existe des acheteurs assez imprudents pour se faire à eux-mêmes l'application d'un remède sur le seul vu de l'indication de ses vertus thérapeutiques, ne suffira-t-elle pas à conduire certains consommateurs à faire du produit qu'ils acquièrcent, un usage inconsidéré? Le public n'est pas sans savoir, au moins vaguement, que tel produit est un remède à telle affection? Cette connaissance sommaire ne suffira-t-elle pas à l'amener à se passer du médecin, tout comme le pourrait faire l'indication ou la simple allusion(car la proposition va jusqu' à interdire une simple allusion) à la vertu thérapeutique du produit?

Quant à nous, cette crainte nous parait chimérique et nous ne voyons qu'une inutile entrave au choix de la marque, dans la disposition que nous examinons.

V

En résumé, seule la proposition relative à la prohibition des marques déceptives, c'est à dire de celles susceptibles de créer une confusion sur la nature du produit nous parait utile et bonne dans son principe.

Mais son adoption, au moins pour bon nombre de législations, serait chose superflue car elle est déjà contenue implicitement dans des prohibitions plus larges et qui s'appliqient aux produits de toute nature.

LEGISLATION INTERNATIONALE SUR L'IMPORTATION DES PRODUITS REVETUS D'UNE MARQUE DE COMMERCE

PAR ANDRE ALLART

Docteur en Droit, Avocat à la Cour d'Appel de Paris

I

Voici comment se pose pratiquement la question: un commerçant qui fait fabriquer les produits qu'il met en vente, dans un Etat autre que celui où est situé son établissement, peut-il y faire apposer sa propre marque de commerce par le fabricant étranger, sans y faire figurer en même temps l'indication du lieu de fabrication de ces objets? Pour prendre de suite un exemple qui éclaire d'un mot la position de la question, un magasin de vente français, tel que *le Louvre,* qui fait fabriquer en Angleterre, certains produits qu'il offre au public, en France, peut-il faire apposer sur ceux-ci par le fabricant étranger, ou apposer lui-même, la marque, "Au Louvre-Paris," sans y joindre la mention *importé d'Angleterre, fabrique en Angleterre,* ou toute autre équivalente?

On sait que la plupart des législations prohibent actuellement les fausses indications de provenance et que les conventions internationales en matière de propriété industrielle ont consacré cette prohibition.

Doit-on considérer une simple marque de commerce, comme pouvant constituer une fausse indication de provenance? A prendre la réalité des choses, il faudrait répondre négativement: car la marque de commerce n'est point le signe du fabricant, mais uniquement celui du vendeur. Son apposition ne devrait donc avoir aucune signification en ce qui touche la provenance des produits qui en sont revêtus. Cependant, dans un désir, peut-être excessif, de sauvegarder le public contre toute confusion, on en est venu, dans la plupart des pays, à considérer comme illicite l'apposition d'une marque de commerce sur des produits de fabrication étrangère.

II

Au point de vue international, la question trouve sa solution dans la Convention d'Union du 20 mars 1883, article 10, qui dispose: "Les dispositions de l'article précédent (saisie à l'importation) seront applicables à tout produit portant faussement, comme indication de provenance le nom d'une localité déterminée, lorsque cette indication sera jointe à un nom commercial fictif ou emprunté dans une intention frauduleuse." Ainsi, il faut, pour que le produit revêtu d'une fausse indication de provenance soit saisi en vertu de cette disposition, ou bien qu'il porte un nom commercial fictif, c'est à dire un nom autre que celui du fabricant ou du vendeur, ou un nom emprunté dans une intention frauduleuse.

Par suite le fait qui nous préoccupe ne rentre pas dans les prévisions de cet article, puisque nous supposons par hypothèse que la marque de commerce apposée sur le produit est bien celle de celui qui le met en vente. On ne peut donc dire qu'il y ait, en l'espèce, apposition d'un nom commercial fictif ou emprunté dans une intention frauduleuse. Ainsi l'importation n'est point prohibée dans ce cas aux termes de la Convention.

Mais il faut noter que la Convention constitue un minimum de protection qui laisse libre champ à l'application de la loi intérieure de chaque pays. Les objets fabriqués à l'étranger et revêtus seulement d'une marque de commerce pourront être saisis à l'importation, si la législation du pays où a lieu cette dernière, considère le fait comme illicite. Notons qu'il en est ainsi en France et en Angleterre, pour ne citer que des exemples.

La Convention de Washington en 1911 n'a rien ajouté au texte de l'article 10 sur ce point.

III

Parmi les Etats signataires de la Convention d'Union, un certain nombre se sont groupés en une Union restrainte et ont signé un arrangement à Madrid le 15 Avril 1891 relatif aux fausses indications de provenance.[1]

[1] Font partie de l'Union restreinte: Le Brésil, Cuba, L'Espagne, la France, la Grande-Bretagne, Le Portugal, la Suisse et la Tunisie.

L'article 3 de cet arrangement vise expressément notre question en disposant: "*Les présentes dispositions ne font pas obstacle a ce que le vendeur indique son nom ou son adresse sur les produits provenant d'un pays différent de celui de la vente; mais dans ce cas l'adresse ou le nom doit-être accompagné de l'indication precise et en caractères apparents, du pays ou du lieu de fabrication ou de production.*"

Ainsi, aux termes de cette disposition, l'importation de produits fabriqués à l'étranger et revêtus de la marque de commerce d'un vendeur établi dans un autre pays; n'est licite qu'à la condition que le lieu de provenance figure en même temps sur le produit.

La sanction de cette disposition est la saisie du produit à l'importation ou la prohibition d'importation (Art. 1.).

IV

Ainsi il existe, au point de vue international, deux systèmes. L'un établi par la Convention d'Union du 20 mars 1883 qui ne s'oppose aucunement à l'introduction des produits revêtus de la marque de commerce d'un négociant établi dans un autre pays que celui d'origine. L'autre édicté par l'arrangement de Madrid, exigeant l'indication du lieu de provenance. Au premier l'on peut reprocher d'être trop large et au second de ne l'être pas assez.

Ce qui rend particulièrement délicate la solution de cette question, c'est que les espèces dans lesquelles elle se présente pratiquement sont des plus variables et ne comportent que difficilement une solution uniforme.

En soi, l'apposition d'une marque de commerce sur un produit ne prouve aucunement que le lieu de provenance du produit soit le lieu indiqué par cette marque. Celle-ci ne se réfère en effet qu'à l'établissement où est vendu le produit et non à celui où il est fabriqué. D'où il suit que la marque de commerce étant tout-à-fait étrangère à la fabrication de l'objet, ne peut en raison être considérée comme une indication de provenance.

On doit en outre observer que beaucoup d'acheteurs ne se préoccupent en aucune façon de l'origine du produit qu'ils achètent. Ils font confiance à un établissement commercial qui leur offre toute garantie que les produits mis en vente par lui sont de bonne qualité. Peu leur importe dès lors que ces produits soient d'une provenance ou d'une autre: le public se trouve suffisamment protégé par la réputation de la maison qui les met en vente. Il ne court donc aucun danger et on le protège malgré lui quand on impose au vendeur l'obligation d'indiquer sur chaque objet quelle en est l'origine.

Obliger le commerçant à mettre cette indication, n'est-ce pas dès lors une entrave inutile à sa liberté? N'est-ce pas vouloir attacher à chaque objet qu'il met en vente, comme un signe destiné à le discréditer, en éveillant les suspicions du public, cette indication de provenance qui souvent lui est si indifférente?

Cela est-il conforme à la liberté des transactions internationales?

Par contre, on fait observer que tous les acheteurs ne manifestent pas ce désintéressement quant à la provenance des produits qui leur sont offerts. La marque de commerce ne se différencie par aucun signe visible de la marque de fabrique: elles pourront-être aisément prises l'une pour l'autre. Si pour certains établissements dont la réputation est considérable, on sait qu'ils sont seulement des établissements de vente mais qu'ils ne fabriquent pas eux-mêmes, et si pour les objets revêtus de leur marque de commerce aucune erreur ne peut naître dans l'esprit du public, il n'en est pas toujours ainsi.

Il existe même des établissements mixtes qui ne fabriquent qu'une partie des objets qu'ils offrent au public, faisant venir les autres de fabriques étrangères. Ici, la confusion n'est-elle pas à redouter de la part des acheteurs et n'est-il pas bon d'avertir ces derniers des origines diverses des objets que leur offre l'établissement auquel ils s'adressent? Comme on peut s'en rendre compte, par ce très bref aperçu, la question demeure fort délicate à résoudre en un principe unique.

V

En ce qui concerne les préparations chimiques une difficulté nouvelle surgit. Fort souvent, les produits mis dans le commerce sont d'une composition complexe et renferment plusieurs éléments. Il arrive que tous n'aient pas la même provenance: l'un est préparé dans un pays, l'autre dans un autre. En cet état ils sont expédiés à un industriel qui leur donne une forme définitive, les combine entre eux et les offre ensuite au public.

Exigera-t-on que celui-ci, outre sa marque propre, indique sur ces produits le lieu d'origine de chacun des éléments entrant dans leur composition? On devrait le faire, si l'on voulait appliquer à la lettre le texte de l'article 3 de l'arrangement de Madrid.

Mais n'y a-t-il pas dans une pareille obligation une entrave excessive à la liberté du commerce et une source de difficultés sans nombre?

VI

En présence de ces diverses considérations, nous inclinerions à émettre un voeu qui constitue un moyen terme entre le système, peut-être trop large, de la Convention de 1883 et celui, trop rigoureux, de l'arrangement de Madrid. Le but de la répression des fausses indications de provenance est la sauvegarde du public. Il faut que celui-ci soit préservé contre la tromperie. Lorsqu on ne cherche pas à la tromper, il n'a besoin d'aucune protection. Le commerçant qui appose sa marque sur un produit de provenance étrangère, ne commet aucune tromperie, car la marque qu'il appose n'est pas l'indication d'une provenance, mais celle d'une maison de vente. Le public, s'il a un doute, et s'il veut s'assurer de manière précise de la provenance du produit qu'il acquiert, aura pour le faire de faciles moyens d'investigation. Il pourra tout d'abord rechercher, s'il ne le sait déja, s'il se trouve en présence d'une marque de fabrique ou d'une marque de commerce. Il pourra ensuite, s'il subsiste un doute dans son esprit, s'enquérir de la provenance du produit et, au besoin, se la faire certifier. S'il ne le fait pas, c'est que la chose lui est indifférente, et alors il n'y a pas lieu d'être plus prévoyant pour lui qu'il ne l'est lui-même.

Nous émettons donc ce voeu:

"que l'apposition d'une marque de commerce sans aucune indication de provenance, par un établissement qui fait venir ses produits de l'étranger, soit déclarée licite, d'une part toutes les fois que cette marque est celle d'un établissement exclusivement commercial et qui ne fabrique aucun produit; d'autre part toutes les fois que cette marque ne porte aucune indication trompeuse destinée à créer une erreur dans l'esprit de l'acheteur."

NECESSITE D'ACTIVER LA SOLUTION DES PROCES CONCERNANT LA PROPRIETE INDUSTRIELLE

PAR A. HUSSON
Paris, France

Depuis longtemps on se préoccupe beaucoup de la situation déplorable que fait, aux industriels comme aux commerçants, l'excessive durée des procès concernant la Propriété Industrielle. Se prolonger pendant quatre ou cinq années, du jour de l'assignation à celui d'une décision définitive, ce n'est point, pour un débat judiciaire visant cette propriété, quelque chose d'extraordinaire. Or, c'est évidemment beaucoup trop; surtout en matière de brevets: car un brevet n'a qu'une existence assez courte et, d'ordinaire, son exploitation n'est guère productive pendant les premières années. Aussi, a-t-on pu dire, avec raison, que les procès nécessités pour la défense d'un brevet durent souvent, pour le breveté, plus longtemps que le brevet lui-même.

Ces préoccupations existent-elles au même degré dans tous les pays? Nous ne connaissons pas assez les différents systèmes de procédure usités dans certaines contrées pour pouvoir l'affirmer. Mais il nous semble qu'en général les brevetés ne sont pas, dans les principaux pays, mieux partagés qu'en France. C'est ainsi que déja, en Allemagne, d'excellents eprits ont préconisé l'organisation de tribunaux mixtes offrant aux plaideurs, avec la garantie d'une compétence plus éclairée, l'assurance d'une parfaite rapidité.

Cette question est d'un intérêt pratique tel que l'Association Française pour la protection de la Propriété Industrielle s'en est déja, plusieurs fois, occupée.

Fondée depuis 1899, comprenant comme adhérents des industriels, des commerçants, des ingénieurs-conseils en matière de propriété industrielle, des avocats spécialistes, des sénateurs, des députés, des Chambres de Commerce, des Chambres Syndicales, etc., cette association a su conquérir rapidement, auprès des Pouvoirs Publics Français, une très sérieuse influence.

Ce qu'elle a fait intéressera donc ceux qui s'occupent de la question générale que nous traitons ici.

Tout d'abord, au cours de différentes réunions de l'Association Française, on parla de créer des tribunaux purement techniques. Mais cette réforme parut trop radicale.

Plus tard, en 1909, au Congrès de Nancy, la question fut l'objet de deux rapports également intéressants.

L'un, de Mr. Armengaud jeune, ingénieur-conseil, soumettait l'examen des procès de contrefaçon à un tribunal composé de jurés techniques, sous la présidence d'un magistrat délégué par le président du tribunal civil. Mais, très original, ce projet bouleversait trop l'ordre de choses établis.

L'autre, de Mr. Moret, avocat à la Cour de Cassation, se contentait d'une réforme plus modeste. Il maintenait l'organisation judiciaire actuelle; mais donnait à la procédure une plus grande rapidité, notamment en ce qui concerne la nomination des experts et la durée de leur expertise. Il est vrai qu'il avait le tort de proclamer l'expertise obligatoire par cela seul que l'une des parties en cause l'eût demandée. C'était une mesure évidemment fâcheuse; car le contrefacteur, pour gagner du temps, n'aurait jamais manqué, même dans le cas d'une indisoutable contrefaçon, de solliciter l'expertise.

Finalement, s'inspirant du projet de Mr. Moret, l'Association Française pour la Protection de la Propriété Industrielle adopta (non pas au Congrès de Nancy où la question resta sans solution définitive, mais dans une Assemblée générale du 22 février 1910) le projet de réforme suivant:

1° "Dans toutes les affaires relatives aux brevets, le Président du Tribunal, ou celui de la Chambre saisie de l'affaire, peut, sur la demande de l'une des parties, statuant en état de référé et en audience publique, nommer un ou trois experts; cette demande devra être formée dans les trois mois de l'assignation."

2° "S'il n'est pas ordonné d'expertise, l'affaire doit être jugée dans les six mois de l'assignation. Le tribunal conserve la faculté d'ordonner, après les débats, une expertise."

3° "Les experts sont choisis sur une liste dressée par la commission technique de l'Office National de la Propriété Industrielle sur la présentation faite par la réunion annuelle des présidents des Chambres de Commerce, et par les corps de professeurs des Universités et des grandes écoles techniques; cette liste sera revisée chaque année et comprendra au moins dix personnalités compétentes dans chacune des spécialités adoptées pour la classification des brevets; un règlement d'administration publique déterminera les mode et conditions suivant lesquels la liste des experts sera dressée."

4° "La décision qui ordonne l'expertise désigne un magistrat pour assister aux séances et diriger les opérations; elle fixe la date à laquelle il sera plaidé au fond dans un délai maximum de six mois. Les rapports où seront consignés les dires des parties et les pièces annexes devront être déposés un mois au plus tard avant la date fixée pour la plaidoirie; les dires et les pièces annexes sont dispensés du timbre et de l'enregistrement; ils sont visés ne varietur par les experts et sont déposés au greffe en même temps que le rapport; une copie sur papier libre peut en être délivrée aux parties. Le magistrat directeur peut, soit d'office, soit sur la demande des parties ou des experts, impartir pour le dépôt du rapport un nouveau délai qui, en aucun cas, ne peut dépasser six mois."

5° "Au cas où le rapport n'aurait pas été déposé en temps utile, le tribunal pourra déclarer les experts dessaisis et ordonner qu'il soit passé outre aux débats."

6° "Lorsque le rapport a été déposé, le Tribunal doit, sur la demande d'une des parties, et peut d'office, ordonner l'audition des experts à l'audience. L'audition des experts peut encore avoir lieu, même s'il n'y a pas eu encore de rapport déposé."

7° "Les frais et honoraires des experts sont liquidés par le jugement qui statue au fond, sans qu'il y ait toutefois solidarité de ce chef entre les parties. Mais la décision nommant les experts, ou une ordonnance du président sur demande motivée des experts, pourront obliger le demandeur à fournir caution pour le paiement des dits frais et honoraires."

8° "L'arrêt à intervenir sur l'appel d'un jugement relatif à une question de brevet d'invention devra être rendu dans les six mois de l'acte d'appel; à moins qu'il n'ait été ordonné par la Cour une mesure d'instruction complémentaire, auquel cas le délai sera prolongé de trois mois."

Enfin, en juillet 1911, à Roubaix, dans le Congrès tenu par la susdite Association Française, sous le patronage du Ministre du Commerce et ceux de la Chambre de Commerce de Paris et de la Chambre de Commerce de Roubaix, fut voté le voeu suivant:

"Le Congrès émet le voeu que le Projet de réforme de la Loi Française de 1844 sur les brevets d'invention, déposé par le Gouvernement et impatiemment attendu par les intéressés, soit complêté par l'organisation de la procédure d'expertise, conformément au projet établi par l'Association et soit discuté par le Parlement dans un délai aussi rapproché que possible."

Nous aurions voulu pouvoir enregistrer le vote d'un voeu quelconque formulé par l'Association *Internationale* pour la Protestion de cette Propriété (Association qui groupe, dans ses Congrès annuels, un grand nombre d'adhérents et d'Associations Nationales, parmi lesquelles, précisément l'Association Française susnommée); mais la question qui nous occupe n'a point encore, jusqu'à ce jour, fixé son attention.

Peut-être, au surplus, avisée elle l'est de toutes les motions discutées dans les différents Congrès Internationaux, au point de vue législation, nous saura-t-elle gré d'avoir pris, *internationalement*, l'initiative de cette réforme et la fera-t-elle entrer, bientôt, dans le programme de toutes celles qu'elle poursuit?

Quoi qu'il en soit, revenons au voeu formulé par l'Association Française et dégageons en les idées gênérales qui nous paraissent devoir répondre aux désiderata de quiconque, Allemand, Américain, Anglais, Espagnol, Français, Italien, Russe, ou autre, plaide pour la défense de la Propriété Industrielle.

Ces idées générales se résument en des mesures que toute législation sur la matière nous semble pouvoir adopter. Ces mesures ont, en effet, pour objet:

d'enlever aux plaideurs la faculté (dont ils abusent trop souvent) de ne demander une expertise qu'après avoir, par des incidents multiples, prolongé les débats inutilement;

de contraindre en outre ces plaideurs à garantir, d'avance, le paiement des dépenses occasionnées par l'expertise qu'ils sollicitent;

d'obliger l'expert, l'avocat, le tribunal, et même la Cour en cas d'appel, à hâter, chacun dans sa sphère, la solution des débats engagés;

de donner à l'expertise plus d'autorité, en permettant la comparution de l'expert à l'audience;

d'assurer enfin plus régulièrement la taxe des frais et honoraires de cet expert.

Inutile, pensons nous, d'insister sur l'avantage de pareilles mesures. Nous souhaiterions seulement:

1° que le dépôt d'une caution par la partie qui requiert l'expertise fût obligatoire et non pas seulement facultatif:

2° que, dans le cas d'appel, l'appelant fût obligé de déposer au greffe de la Cour une somme déterminée par le Président de celle-ci, somme garantissant, tout au moins, le paiement des nouveaux frais dont cet appel va grever la procédure. Mais peut-être pensera-t-on que la proposition de cette mesure, apportant une véritable restriction au droit d'appel, risquerait de compromettre l'adoption du voeu plus modeste formulé par l'Association Française et dont nous proposons au Congrès d'adopter internationalement les idées générales.

En conséquence, nous avons l'honneur de soumettre au vote du Congrès la proposition suivante:

a. Dans tout procès intéressant la Propriété Industrielle, le plaideur qui désire une expertise doit la demander dans les 3 mois qui suivent l'assignation.

b. En l'absence d'expertise, le Tribunal doit statuer dans les 6 mois de l'assignation. Mais il est libre d'en ordonner une, après les débats, s'il n'est pas suffisamment éclairé.

c. En cas d'expertise, les parties doivent plaider au fond dans les 6 mois du jugement qui a ordonné celle-ci (délai maximum).

d. Sous peine de dessaisissement, l'expert doit déposer son rapport 1 mois, au plus tard, avant la date fixée pour les plaidoiries. Cependant, le Tribunal peut lui accorder un sursis de 6 mois (délai maximum).

e. Obligé d'ordonner (avant ou après le dépôt de leur rapport) l'audition des experts à la barre, si elle est requise par une des parties, le Tribunal est libre de l'ordonner d'office s'il le juge nécessaire.

f. Le plaideur qui requiert une expertise est obligé de garantir par une caution le paiement des frais de l'expertise (y compris les honoraires de l'expert).

g. En cas d'appel, la Cour doit statuer dans les 6 mois de celui-ci (sauf prorogation de 3 mois si elle a ordonné quelque mesure supplémentaire d'instruction).

LA FABRICATION DANS UN PAYS DE LA CONVENTION INTERNATIONALE DE LA PROPRIETE INDUSTRIELLE PROTEGE LE POSSESSEUR D'UN BREVET DANS TOUTES LES NATIONS FAISANT PARTIE DE LA CONVENTION

PAR FERNAND JACQ

Docteur en Droit, Avocat à la Cour de Paris, Paris, France

Aux termes de l'Article 2 du texte encore actuellement en vigueur de la Convention d'Union de 1883 et de l'Acte additionnel de 1900: "Les sujets ou citoyens de chacun des Etats contractants jouiront, dans tous les autres Etats de l'Union, en ce qui concerne les Brevets d'invention.......des avantages que les lois respectives accordent actuellement ou accorderont par la suite aux nationaux. En conséquence, ils auront la même protection que ceux-ci et le même recours légal contre toute atteinte portée à leurs droits sous réserve de l'accomplissement des formalités et des conditions imposées aux Nationaux par la législation intérieure de chaque Etat."

D'autre part l'Article 5 édicte que: "L'introduction par le Breveté, dans le pays où le brevet a été délivré, d'objets fabriqués dans l'un ou l'autre des Etats de l'Union, n'entraînera pas la déchéance. Toutefois, le breveté restera soumis à l'obligation d'exploiter son brevet conformémént aux lois du pays où il introduit les objets brevetés."

Il semblerait donc, à cette simple lecture du texte de la Convention que l'exploitation dans un pays unioniste devrait en principe suffire pour empêcher la déchéance du brevet pour défaut d'exploitation dans les autres pays de l'union où il possède des brevets! Toute la difficulté consisterait alors à savoir ce que veut expressément dire la Convention par le mot "exploitation". Or depuis longtemps la jurisprudence est fixée sur le sens exact à donner au mot "exploitation"; elle considère d'une façon constante qu'il faut entendre par là, non pas une *exploitation commerciale,* mais une *fabrication industrielle!*

Par conséquent, la seule cause de déchéance pour défaut d'exploitation pouvant survenir à l'égard d'un breveté unioniste, ne serait possible que s'il faisait fabriquer totalement ou partiellement (élément essentiel de son invention) dans un pays non unioniste, et se contentait d'exploiter commercialement sur le territoire de l'Union!

Mais l'Article 5 précité, dans son 2° paragraphe, apporte une réserve importante au principe du paragraphe 1°, en déclarant que toutefois le breveté restera soumis à l'obligation d'exploiter son brevet conformément aux lois du pays où il introduit les objets brevetés."

Les conséquences de ce deuxième paragraphe peuvent être considérables et, à l'égard de certaines législations particulières, elles peuvent faire échec complètement au principe général de l'exploitation suffisante dans un seul des pays de l'Union.

C'est ainsi que la Loi Anglaise de 1907 impose, même à l'égard d'un unioniste étranger, l'exploitation principale sur le territoire du Royaume-Uni. La plupart des autres pays imposent également un minimum d'exploitation dans le pays. La Belgique prononce la déchéance (art. 23 de sa loi de 1854) par défaut d'exploitation dans l'année de la mise en exploitation à l'étranger, ou pour interruption pendant un an de l'exploitation en Belgique. Le Brésil rend possible, en cas de fourniture insuffisante pour la consommation interne, la réduction du monopole accordée par le brevet, à une certaine zone. D'autres pays, comme l'Italie, le Pérou, la Roumanie, la Russie, se réservent d'accorder des excuses et des délais de prolongation, etc.....En France, la jurisprudence exige que l'inventeur, pour éviter la déchéance pour non-exploitation, fasse en sorte qu'il n'existe pas une disproportion manifeste entre l'importance de la fabrication effectuée sur le territoire français et celle des introductions de l'étranger, et surtout, s'il s'agit d'un étranger, breveté simultanément en France et à l'étranger, qu'il n'existe pas un contraste trop grand entre l'effort fait à l'étranger pour assurer le développement industriel de l'invention et l'effort corrélatif en France (notamment: Tribunal de la Seine, 30 juin 1897, Bartlett (Jantes métalliques), Annales de la Propriété Industrielle (Recueil Pataille), 1900, p. 275).

Pour conclure: malgré le principe de la Convention (art. 2 et 5 § 1°) l'exploitation, ou plus exactement la fabrication industrielle, dans un des pays de l'Union n'est pas suffisante en général, pour empêcher la déchéance pour défaut d'exploitation dans les autres pays unionistes; car il faut, pour chaque pays, s'en rapporter aux prescriptions expresses de la loi intérieure qui peuvent réduire considérablement et même supprimer en fait le principe libéral du paragraphe 1° de l'article 5.

C'est pourquoi il est désirable de poursuivre dans les divers Congrès l'unification progressive des lois sur les brevets d'invention. En attendant de pouvoir réaliser le brevet international qui mettrait fin à toutes les incertitudes et mieux encore que les réformes successives dans un sens unitaire imposées à force de propagande par les grandes associations spécialistes internationales ou nationales ayant en vue la protection de la propriété industrielle.

Il est donc indispensable que tous les congrès qui, à un point de vue quelconque, s'intéressent à la propriété industrielle, émettent des voeux formels pour la suppression progressive des divergences des législations intérieures, éminemment nocives à l'excercice de plus en plus international du commerce et de l'industrie, et s'efforcent, par une propagande personnelle de leurs membres basée sur un programme commun, d'aider à la réalisation, la plus prochaine possible, de leurs voeux.

LEGISLATION INTERNATIONALE UNIFORME POUR LES BREVETS ET LES MARQUES

Fernand Jacq
Paris, France

Il faut d'abord interpréter le sens exact du sujet proposé; il ne peut être évidemment question d'une législation uniforme à la fois pour les brevets et les marques mais simplement du désir de réaliser éventuellement deux séries de législations internationalement uniformes, l'une pour les brevets et l'autre pour les marques.

En effet si les brevets et les marques constituent deux modes essentiels de la protection de la propriété industrielle et commerciale, ils sont par contre très différents quant à leur domaine et à leur genre d'application. C'est ainsi que le brevet d'invention vise la protection essentiellement technique de procédés d'ordre industriel, tandis que la marque de fabrique, qui n'est, la plupart du temps, qu'un adjuvant du nom du fabricant, est exclusivement d'ordre commercial et protège en quelque sorte extrinsèquement le produit qu'elle recouvre.

On se rend facilement compte d'autre part, à priori, qu'au point de vue économique, la protection obtenue par un brevet d'invention est plus importante et plus délicate que celle octroyée par les marques. Par conséquent, il ne peut être à aucun point de vue question d'essayer de réaliser une loi générale uniforme de la protection de la propriété industrielle englobant à la fois les brevets et les marques; mais il est tout à fait désirable de se proposer comme but, peut-être lointain, mais assurément très possible, deux lois internationales uniques: l'une instituant un brevet d'invention international, et l'autre un statut également international des marques de fabrique.

Pour le brevet d'invention international le rapporteur renvoie à ses conclusions développées sous les questions B et 8 mises à l'ordre du jour du Congrès.

En ce qui concerne l'uniformisation des législations en matière de Marques, la Conférence de Washington de mai 1911 a quelque peu amélioré le régime de la Convention d'Union et des Arrangements Internationaux qui l'ont suivie.

Il n'apparaît pas nécessaire, en dehors de certaines définitions et prescriptions essentielles, de faire une loi internationale uniforme de la marque de fabrique. Il suffit, et c'est l'œuvre progressive des Conférences Internationales, de définir nettement le statut international de la marque, d'uniformiser les formalités d'enregistrement en les réduisant au minimum de publicité nécessaire, de réglementer uniformément les effets du dépôt pour parvenir à réaliser une législation internationale suffisamment uniforme et pratiquement satisfaisante de la marque de fabrique.

Sans s'attacher trop servilement à la terminologie, il faut essentiellement considérer qu'en fait la protection accordée aux marques de fabrique a surtout pour but d'empêcher, sous l'une de ses principales formes, la concurrence déloyale, qui sévit de plus en plus, et qui, au fur et à mesure de l'internationalisation du commerce, devient de plus en plus difficile à réprimer.

Aussi partageons-nous complètement l'avis de l'éminent Secrétaire général de l'Association Internationale pour la Protection de la Propriété Industrielle, le professeur Osterrieth, qui déclare dans son rapport "sur la protection internationale des marques de Fabrique" présenté au Congrès de Londres des 3–8 juin 1912: "Quiconque introduit dans un pays une marque doit être protégé contre toute concurrence déloyale commise au moyen de la contrefaçon de cette marque. L'enregistrement ne sert qu'à faciliter et à renforcer cette protection; refuser la protection à une marque en raison du fait qu'elle n'a pas été enregistrée au pays d'origine, a pour effet de tolérer et même de favoriser la concurrence déloyale. Nous pensons donc que, lorsqu'on reconnaîtra, comme véritable point de départ de la protection des marques, la nécessité de réprimer la concurrence déloyale, on arrivera à admettre qu'il n'est ni nécessaire ni utile de subordonner la protection de la marque à l'accomplissement dans un autre pays d'une formalité, qui n'a aucun intérêt, pour statuer sur des faits de concurrence déloyale."

Il faut donc prendre pour critérium de la protection internationale efficace de la propriété des marques de fabrique tout ce qui est susceptible de réprimer en même temps la concurrence déloyale.

Il suffira par conséqueut à la loi uniforme qui régira éventuellement les marques de fabrique, de porter essentiellement sur les points suivants:

I° Définition internationale unique de la Marque.

2° Indépendance des marques internationales.

3° Modalité uniforme du dépôt (dépôt déclaratif, de préférence à dépôt attributif).

4° Droit de priorité pour le dépôt successif des marques dans chaque pays étendu à un an, comme pour les brevets d'invention, au lieu des 4 mois actuels.

5° Enregistrement international unique suffisant.

6° Protection de la marque telle qu'elle est déposée au pays d'origine.

Il serait excessif de développer ici les raisons qui militent en faveur de l'adoption dans le texte de la Convention d'Union des 6 paragraphes sus-énoncés. Les industriels et commerçants savent par expérience la grande difficulté qu'ils éprouvent actuellement à faire protéger à l'étranger leurs marques personnelles tant à cause des différences du domaine de la marque dans chaque pays, du système de dépôt (attributif ou déclaratif) que des délais d'enregistrement, pour conserver un droit certain de priorité.

La conférence de Washington, malgré les efforts faits par les différents Congrès de la propriété industrielle pour obtenir satisfaction sur ces différents points n'a, à vrai dire, réalisé de progrès que sur la question de la définition de la marque. (Article 6 de la Convention.)

L'article 6 nouveau, en remaniant l'ancien texte, et notamment en supprimant le chiffre 4 de l'ancien Protocole de clôture a réalisé tout au moins implicitement et, pourrait-on dire négativement, la définition internationale de la marque. Or c'est là un résultat considérable, qui constitue un pas décisif franchi dans la voie de l'unification internationale de la législation. C'est un progrès dont les conséquences se feront vraisemblablement prochainement sentir; car, s'il est vrai que la définition implicitement donnée par l'alinéa 2, ne vise que la protection internationale, il est cependant logique d'espérer que les divers pays, grâce a mouvement évolutif constant de la législation, adapteront leurs dispositions internes aux résolutions de la Conférence.

La Conférence, qui ne pouvait adopter que les dispositions présentées à l'unanimité, s'est montrée, dans sa majorité, favorable à d'autres questions importantes, qui sont donc mûres pour une prochaine réunion.

Or, si à la prochaine Conférence on parvient, comme c'est probable, à l'adoption d'un texte encore plus précis, donnant une définition vraiment complète de la marque (c'est à dire protection de tous signes ne *constituant pas la désignation nécessaire* d'un produit et présentant un *caractère distinctif* quelconque), on aura franchi une étape essentielle et décisive de la route vers l'unification complète de la législation.

Toutes les autres questions viendront nécessairement ensuite et en tous cas perdront immédiatement de leur importance, sauf cependant la question de l'effet du dépôt, qui est l'une des plus délicates à résoudre. Sur ce point encore il faut espérer que la logique, aidée des leçons de l'expérience, déterminera les pays à dépôt attributif à abandonner un système injuste et particulièrement défavorable à la loyauté commerciale. Quant à la question du délai de priorité il est vraiment inconcevable que la récente Conférence de Washington ne l'ait pas résolue dans le sens proposé par l'Association Internationale; ce sera certainement fait la prochaine fois.

En résumé, si la réalisation, tout à fait souhaitable, d'une loi instaurant un système de brevet international est encore malheureusement assez lointaine, il en est tout autrement en ce qui concerne l'uniformisation de la législation sur les marques de fabrique; un pas décisif a été franchi par la dernière Conférence Internationale, il appartient aux divers Congrès intéressés de faire la propagande nécessaire pour obliger la prochaine Conférence à réaliser complètement une réforme que l'internationalisation, de plus en plus complète du commerce, réclame impérieusement

LES BREVETS INTERNATIONAUX SONT-ILS DESIRABLES OU NON?

Par Fernand Jacq

Docteur en Droit, Avocat à la Cour de Paris, Paris, France

Quand on a commencé à s'intéresser internationalement à la question de la protection des brevets d'invention, la première idée qui est venue à l'esprit des ingénieurs et des jurisconsultes compétents a été de chercher à élaborer une loi unique, internationale, organisant la protection des inventions brevetées.

A Vienne, en 1873, le premier Congrès de la propriété industrielle a émis un voeu dans ce sens; le Congrès de Paris de 1878 a cherché lui aussi, à élaborer les bases d'un avant-projet portant sur l'instauration d'un brevet international. Un orateur autorisé du Congrès, M. Armengaud jeune, fit alors remarquer que l'idée, judicieuse en elle-même, lui apparaissait tout au moins prématurée quant à sa réalisation; il proposait, en conséquence, de chercher plutôt à établir une protection internationale efficace, des inventions brevetées par la conclusion de traités spéciaux ou mieux d'un traité général entre les Etats intéressés, tout en réservant à chaque pays la faculté d'organiser cette protection conformément à ses vues économiques et juridiques personnelles. La motion de M. Armengaud obtint les suffrages du Congrès qui décida la conclusion prochaine d'une union internationale, réalisée en effet postérieurement en 1883, sous le vocable de Convention internationale de Paris.

Depuis, les propositions de création d'un système de brevet international, reprises officieusement aux divers Congrès successifs pour la protection de la propriété industrielle se heurtèrent au scepticisme de la majorité des congressistes, qui voyaient dans la diversité des lois nationales l'antagonisme des intérêts économiques et l'évolution inégale du développement industriel et commercial dans les divers pays, un obstacle de plus en plus insurmontable à l'établissement d'une loi internationale unique organisant le régime des brevets d'invention.

Le huitième Congrès international de chimie appliquée, tenu à Londres en juin 1909, repris, sur la proposition de plusieurs de ses membres, l'idée du brevet international et décida de nommer une commission chargée d'étudier la question d'une manière approfondie et de présenter un avant-projet, qui pût être discuté au prochain Congrès de chimie appliquée, prévu pour juin 1912 à Washington. La même année, le 13° Congrès de propriété industrielle réuni en Octobre à Nancy, reprit à son tour, sur l'initiative du professeur Osterrieth de Berlin, l'idée du brevet international.[1] M. Osterrieth signalait, en effet, la nécessité d'uniformiser progressivement, et sur les points essentiels tout au moins, le régime de la protection industrielle notamment en ce qui concerne les brevets d'invention. Le Congrès, disait-il, a demandé la suppression internationale de l'obligation d'exploiter, mais il faudrait également uniformiser le mode de délivrance des brevets. Or, c'est une tache ardue et délicate; les principaux pays, en effet, pratiquent à cet égard les modes les plus différents. La France n'a pas d'examen préalable; l'Allemagne, au contraire, a créé un office d'examen très sévère, le "Patentamt"; l'Angleterre a adopté le système de l'avis préalable; quel système choisir pour l'imposer internationalement? La question est d'autant plus troublante qu'un mouvement semble se dessiner en France (proposition Astier) en faveur de l'instauration d'un régime d'examen préalable. Cependant, le mouvement en faveur de la création d'un Office d'examen préalable est plus apparent que réel; il n'a de partisans déterminés que dans certains milieux, où il est de principe de trouver toujours plus parfaite l'organisation des autres: l'immense majorité des gens compétents y est formellement opposée; et, en Allemagne, les personnalités les plus compétentes manifestent une hostilité grandissante contre l'organisation du "Patentamt," d'autre part, abandonnant son libéralisme traditionnel, l'Angleterre vient d'adopter le régime de l'avis préalable! En Amérique, enfin, il est indéniable qu'une réaction progressive se dessine contre le système de l'examen préalable.

Le professeur Osterrieth proposait en conséquence de laisser subsister les Cours d'examen existantes (Patentamt, Patent-Offices) comme institutions scientifiques techniques (examinant facultativement et postérieurement à leur délivrance le merite des inventions) et de les considérer comme des institutions dépendant d'une Cour suprême internationale d'examen à créer éventuellement.

---

[1] V. Annuaire de l'Ass. int., 1909, p. 159 et suiv.

Il concluait en demandant la nomination d'une commission d'études chargée d'examiner et de comparer les diverses lois des divers pays, dans leur évolution historique et au triple point de vue économique, social et jurdique, afin de pouvoir rédiger, tout au moins sur les questions essentielles, un projet susceptible de recueillir l'agrément unanime. La proposition Osterrieth fut adoptée à l'unanimité et inscrite à l'ordre du jour du Congrès de Bruxelles de juin 1910. La question fit l'objet de deux intéressants rapports, l'un de M. de Snyers, l'autre de M. de Laire, tous deux ingénieurs, favorables au brevet international;[1] et le Congrès chargea en conséquence une commission d'études d'entreprendre l'examen appronfondi d'un projet de brevet international sur un programme très détaillé.[2]

Dans le même esprit, et en vue de centraliser internationalement les services de la propriété industrielle, le professeur Osterrieth, rappelant le voeu exprimé par le Congrès de chimie appliquée réuni à Rome en 1906, faisait adopter par le Congrès de Bruxelles le voeu suivant:

Que la conférence de Washington rappelle au Etats signataires leur obligation contractuelle de mettre leur législation en accord avec la convention, notamment l'obligation pour chacun d'eux, de créer un service spécial de la propriété industrielle dans les conditions prévues par l'Article 12 de la Convention d'Union; que en outre, la Conférence de Washington émet le voeu que les descriptions et dessins des brevets dans tous les Etats de l'Union soient publiés sous forme de fascicules séparés et mis en vente à un prix modique.

D'autre part, M. Schwaerbsch, ingénieur-conseil, directeur du Bureau d'informations pour la protection de la propriété industrielle à la "Royal Wurtembergische Zentralstelle für Gewerbe und Handel" à Stuttgart, signalant la nécessité de créer un office international susceptible de renseigner économiquement les intéressés sur les diverses questions se rapportant aux brevets d'inventions, indiquait que le premier essai de création d'une institution officielle de ce genre avait été fait en octobre 1908 par la "Royal Wurtembergische Zentralstelle für Gewerbe and Handel," laquelle fonda un Bureau public d'informations pour la protection de la propriété industrielle, ce Bureau étant organisé et dirigé au début par un agent de brevets. La création de ce Bureau avait, en effet, paru indispensable à la suite des plaintes nombreuses de personnes peu fortunées, qui tombaient fréquemment entre les mains d'individus malhonnêtes, lesquels abusaient d'elles, soit en obtenant leurs brevets, soit en négociant à leur insuleurs droits privilégiés. Au début, on avait pensé à donner des conseils entièrement gratuits, sans se soucier de la situation personnelle des intéressés, puis on réclama des subsides modérés aux industriels aisés. Ce fut un succès: l'institution en une année à peine répondit, en effet, oralement à 80 demandes et par écrit à 672; c'était la preuve du besoin longtemps ressenti auquel elle venait de donner satisfaction.

---

[1] V. Annuaire d'Ass. int., 1910 p. 236 et 242.

[2] Au mois de Septembre suivant, le Congrès international des Associations d'Inventeurs et des Associations d'Artistes industriels décidait également l'étude, par une Commission compétente de la question du brevet international. V. Annuaire Ass. Inter. p. 248.

Puis l'Office fut obligé d'étendre son champ d'action en s'adjoignant un jurisconsulte, de façon à pouvoir assister les personnes inexpérimentées et à leur procurer la protection de la loi, soit en réclamant la restitution de l'argent indûment perçu, soit en réprimant le tort qui leur avait été fait, soit enfin, au commencement de l'année 1910, le Bureau d'informations avec le concours d'un grand nombre d'agents de brevets organisa une exposition universelle d'inventions pour faciliter aux brevetés la vente de leurs brevets ou la concession de licences d'exploitation.

Dans l'état actuel des choses, tant en Allemagne qu'ailleurs, il serait désirable de généraliser l'arrangement réalisé par la "Royal Zentralstelle de Wurtemberg", conformément aux circonstances et exigences spéciales de chaque pays, en instituant un office quelconque, soit dépendant, soit indépendant d'un service gouvernemental, dans le but de fournir des informations et des conseils en matière de propriété industrielle et dont la direction serait confiée à des personnes expérimentées.

Indépendamment de son but philanthrotopique, cette organisation généralisée constituerait un véritable Office de brevets susceptible de rendre de grands services et d'aider, par l'étroite solidarité des bureaux entre eux, à la centralisation internationale des services de la propriété industrielle et, par conséquent, à la préparation à l'unification de la législation.

La commission instaurée par le Congrès de Bruxelles s'est mise immédiatement à l'œuvre, elle s'est divisée en un certain nombre de sous-commissions, dans chacun des principaux pays reliées entre elles par un comité central destiné à centraliser les documents et à préparer éventuellement un avant-projet, mais la besogne est ardue et l'on ne peut prévoir de résultats avant plusieurs années de laborieuses études.

En dehors de cette activité en quelque sorte officielle, il y a eu des initiatives particulières. C'est ainsi que, tout récemment, un industriel, M. Julien Bernard saisissait le ministère du Commerce d'une proposition (d'ailleurs déjà présentée à maintes reprises) visant l'institution du brevet international. Le système préconisé par M. Julien Bernard consiste à organiser le dépôt unique par voie postale à ce qu'il appelle un "Central Mondial." L'inventeur, désireux d'être protégé internationalement, adresserait une demande accompagnée d'une note explicative au Bureau international compétent, lequel procéderait à l'examen de la demande; cet examen unique serait limité à la nouveauté de l'invention et effectué par une commission internationale; une patente de propriété, valable dans tous les pays, serait accordée à l'inventeur (brevet international), mais ce brevet n'attribuerait pas à son propriétaire de monopole exclusif d'exploitation et ne pourrait faire obstacle à la libre exploitation de son invention dans l'industrie, il percevrait seulement sur les objets fabriqués une redevance déterminée et à charge encore d'en remettre partie à l'Etat (probablement du pays d'origine du demandeur).

M. Julien Bernard prévoit, en outre, pour la perception de cette redevance l'apposition de poinçons et marques sur les objets fabriqués, et la création, pour assurer cette perception, d'une association mondiale de défense des auteurs industriels.

En dehors des difficultés matérielles d'organisation, il est à peine besoin de faire remarquer ce qu'a d'utopique et même de dangereux la conception de M. J. Bernard. Elle lèse intérêts mêmes qu'elle prétend défendre, puisqu'elle dépouille l'inventeur du droit de disposer librement de son invention et accepte sans réserves le fonctionnement automatique ce la licence obligatoire qui constitue une atteinte considérable au droit de l'inventeur et en est en quelque sorte la négation.

Le projet de M. J. Bernard, si intéressant qu'il soit comme tentative de principe pour réaliser une protection internationale à la fois plus facile, plus rapide et moins coûteuse des inventions, qu'apparemment compétent pour résoudre une question aussi complexe.

Le brevet unique international est assurément le but que doivent se proposer tous ceux qui s'intéressent à la propriété industrielle, mais il y a loin de la coupe aux lèvres! Il y a des difficultés considérables à vaincre. Il faut d'abord s'astreindre à diminuer les divergences considérables des législations, qui portent sur des points importants du régime des brevets; il y en a d'anodines, mais il y en a aussi de presque insurmontables. C'est ainsi qu'en ce qui concerne le caractère de brevetabilité, les différences de conception et de définition ne présentent qu'un intérêt secondaire, et l'on pourrait facilement arriver à l'admission d'un principe commun; d'ailleurs, à cet égard, les conventions internationales peuvent réaliser immédiatement l'unification.[1] Par contre, il existe des divergences profondes, notamment dans la conception du mode de délivrance des brevets.

Le brevet international se comprendrait assez facilement dans le système de non examen préalable; au contraire avec le système de l'examen préalable, il faudrait constituer pour cet examen un organisme central extrêmement compliqué et coûteux, et dont les décisions risqueraient fort de ne pas être acceptées sans appel par les différents intéressés.

Le Patentamt allemand, malgré sa puissante organisation, son perfectionnement continu, les énormes crédits dont il dispose, se montre chaque jour plus impuissant à remplir la tâche qui lui est imposée, et celà suffit à souligner les difficultés qu'il y aurait à établir un organe unique d'examen pour les inventions du monde entier.

---

[1] Les diverses Conventions internationales ont en effet unifié déjà, sur des points importants, le lois des divers pays sur les brevets et tout récemment encore la Conférence de Washington.

Il n'y a donc pas lieu pour le moment de tenter la réalisation immédiate du brevet international, ce serait aller à un échec certain; mais, loin cependant d'en abandonner le principe, il faut tout au contraire encourager les associations spéciales, s'occupant de la question, dans le travail d'unification des lois internes qu'elles poursuivent déjà depuis de longues années. Cette unification par étapes successives conduira fatalement au système du brevet international.

Il faut aussi attendre avec intérêt le résultat des travaux de la Commission d'études de l'Association internationale pour la protection de la propriété industrielle: ce n'est donc pas avant plusieurs années que l'on pourra, semble-t-il, parler avec quelque précision, de projets de brevet international et il faudra alors les discuter internationalement et se mettre d'accord sur ces textes; on peut dire sans crainte que la réforme est encore d'une réalisation lointaine.

MISE EN OEUVRE OBLIGATOIRE DES INVENTIONS ET LICENCE OBLIGATOIRE

PAR FERNAND JACQ

Docteur en Droit, Avocat à la Cour de Paris, Paris, France

Aux termes de l'art. 32, §2, de la loi du 5 juillet 1844, modifié par la loi du 20 Mai 1856, le breveté "qui n'a pas mis en exploitation sa découverte ou invention en France dans le délai de 2 ans, à dater du jour de la signature du brevet, ou qui a cessé de l'exploiter pendant deux années consécutives, à moins que, dans l'un ou l'autre cas, il ne justifie des causes de son inaction" est déchu de ses droits privatifs; la loi du 1° juillet 1906 (pour rendre possible l'application de la Convention d'Union de 1883 (protocole de clôture, art. 3 bis) auquel la France avait adhéré, et qui étend le délai à trois années) a décidé que les Français pourraient revendiquer l'application à leur profit des dispositions de la Convention... dans tous les cas où ces dispositions sont plus favorables à l'inventeur que la loi française et notamment...en ce qui concerne les délais d'exploitation en matière de brevets d'inventions.

La déchéance pour défaut d'exploitation dans un délai maximum variant de 2 à 5 ans, existe dans la plupart des législations, elle a été diversement appréciée depuis qu'elle fonctionne, mais, malgré les critiques nombreuses auxquelles elle a donné lieu, elle a été généralement maintenue dans les divers pays qui ont adhéré à la Convention d'Union de 1883.[1]

---

[1] Cette assertion n'est toutefois rigoureuse que dans sa généralité; jusqu'en 1907, l'Angleterre n'admettait pas la déchéance pour défaut d'exploitation, elle se bornait à décider que le breveté, qui s'abstenait d'exploiter, devait être soumis à la licence obligatoire. Rompant brusquement avec son passé libéral, et contrairement aux principes admis par l'Association Internationale industrielle, le Parlement Anglais a voté, le 28 août 1907, une loi nouvelle qui décide, art. 27 que: "chacun peut, en tout temps, après qu'il se sera écoulé quatre ans depuis la date d'un brevet ou un an au moins après l'adoption de la présente loi, adresser au contrôleur une demande de révocationde ce brevet, basée sur le fait que l'article ou le procédé breveté est exclusivement ou principalement fabriqué ou exploité hors du Royaume-Uni." Par contre le Reichstag Allemand par une loi en date du 6 juin 1911, entrée en vigueur le 1° juillet suivant, dispose que "lorsque le breveté se refusera à accorder à un tiers le droit d'employer l'invention même moyennant une rémunération convenable

C'est pour la première fois, semble-t-il, au Congrès International de la propriété industrielle tenu en 1897 à Vienne que s'est posée avec intérêt la question de la suppression de l'obligation d'exploiter. Le Congrès se termina après une longue discussion par l'adoption, à une caractéristique majorité, d'un voeu demandant sa suppression.[1] Repris en 1898 au Congrès de Londres, le voeu émis par le Congrès de Vienne recueillit cette fois des suffrages unanimes[2] mais c'est à Paris, au Congrès tenu du 23 au 28 juillet 1900 que a question de la suppression de l'obligation d'exploiter donna lieu à la plus intéressante discussion.

Deux rapports remarquables[3] l'un de M. G. Huard, avocat à la Cour de Paris, l'autre de M. Von Schütz, directeur de la Fried Krupp Gruson Werk, concluaient nettement à la suppression de l'obligation d'exploiter quelle qu'en fût la sanction, déchéance pure et simple ou licence obligatoire, et le rapporteur génèral G. Maillard, adoptant les conclusions Huard et Von Schütz faisait adopter à l'unanimité le principe précédemment admis à Vienne et à Londres: "Il est nécessaire dans l'avenir d'abandonner en principe l'obligation d'exploiter." Puis ajoutant aux conclusions des rapporteurs il indiquait, pour remédier à l'inconvénient qui lui semblait résulter de la liberté de ne pas exploiter, (notamment dans la crainte qu'un inventeur étranger, venant se faire breveter en France et ne voulant pas exploiter ne pût interdire à l'industrie française de profiter d'un progrès réalisé à l'extérieur) il proposait d'organiser un système de licences obligatoires, dont le principe était également admis par le Congrès, mais sans préciser le mode d'application.

---

et une garantie suffisante, l'on pourra, si l'intérêt public paraît l'exiger, concéder à ce tiers le droit d'utiliser l'invention (licence obligatoire)... le brevet pourra être révoqué quand l'invention aura été exécutée exclusivement ou principalement hors de territoire du l'Empire Allemand." L'Allemagne reprend donc en quelque sorte à l'Angleterre, qui l'abandonne, le système de la licence obligatoire qui atténue les conséquences de la déchéance pure et simple pour non-exploitation. La Finlande et la Suède corrigent la rigueur de la déchéance pour non-exploitation dans le délai imparti par la concession de licences obligatoires à des tiers. Le Mexique n'exige pas l'exploitation par le breveté, mais organise le fonctionnement automatique, à l'expiration du terme prévu, de la licence obligatoire. Le Venezuela n' exige qu'une exploitation unique, soit à l'intérieur, soit à l'extérieur de la République. Aux Etats-Unis, l'obligation d'exploiter n'existe pas.

[1] V. *Annuaire de l'Assoc. Int. Ind.* 1897, p. 65–69.

[2] V. *Ibid.* 1898, p. 54 et suivantes.

[3] V. *Bull. de l'Assoc. franç. pour la protection de la propriété industrielle* 1902, p. 84 et suiv.; V. aussi *Ibid.* la discussion de ces rapports, p. 262 et suiv.

Une sous-commission fut chargée d'étudier la rédaction d'un texte plus explicite. L'un des membres de cette sous-commission M. Moulton, célèbre avocat Anglais, y vint déclarer que, si la licence obligatoire était excellente en théorie, elle rencontrait dans l'application des difficultés considérables; que notamment en Angleterre on avait essayé d'établir un système de licences obligatoires plus complet que celui alors en vigueur dans ce pays, et qu'aprés une étude et des discussions minutieuses on avait abandonné le projet. Un autre membre de la sous-commission, le Professeur Bernthesen, délégué de la Badische Anilin und Soda Fabrick se déclara également très partisan du principe de la licence obligatoire, mais il considérait comme très difficile, de déterminer dans quelles conditions le prix de ces licences serait fixé, et de trouver un tribunal présentant une compétence suffisante pour apprécier la valeur d'une invention et contraindre la breveté à accorder licence à un concurrent avec lequel il n'avait pu préalablement s'entendre. Aussi la sous-commission jugeat-elle à propos de ne voter que la mise à l'étude de la licence obligatoire et de maintenir dans sa généralité et son imprécision voulues le voeu émis par le Congrès.

Les Congrès Internationaux postérieurs (successivement tenus à Düsseldorf, Amsterdam, Turin, Stockholm, Liège, Berlin, Cologne, Copenhague) ont toujours maintenu avec la même unanimité le principe de la suppression de l'obligation d'exploiter, sans arriver par contre à se mettre d'accord sur un système définitif de licence obligatoire.

Au Congrès de Nancy de 1909, au lendemain de la nouvelle loi anglaise, qui rétablissait l'obligation d'exploiter, la question prit un caractère prépondérant. Si intéressante qu'en fût la discussion, il serait excessif de la prétendre consigner ici, même succintement analysée;[1] il suffira de rappeler les conclusions du rapporteur général G. Maillard:

"Depuis le Congrès de Vienne de 1897, déclarait-il, il y a accord unanime pour supprimer l'obligation d'exploiter avec cette constatation qu'elle ne peut avoir comme sanction pratique l'obligation d'exploiter, mais il a été impossible d'établir un projet international pour organiser judicieusement son fonctionnement."

[1] V. *Bull. de l'Assoc. Intern. Industr.* 1909, p. 104 et suiv.

En France, la question, très soigneusement étudiée, a été l'objet d'un projet de loi[1] préparé par M. A. Taillefer, avocat à la Cour de Paris et voté à l'unanimité par l'Association Française pour la protection de la propriété industrielle, mais le projet n'a pas été agréé par le Gouvernement français.[2] Il semble cependant que les critiques qu'a soulevées l'application de la nouvelle loi anglaise conseille de persister plus que jamais dans la suppression de l'obligation d'exploiter et il convient de profiter de la prochaine réunion de la Conférence de Washington pour la révision de la Convention d'Union[3] pour que cette question soit reprise à la Conférence et enfin solutionnée, il serait donc indispensable de se mettre d'accord sur un texte unique acceptable par tous les pays de l'Union, ce qui devrait être relativement facile puisque la plupart des pays unionistes ont engagé entre eux des pourparlers à ce sujet.

Il faudrait chercher à obtenir à défaut de la suppression pure et simple de l'obligation d'exploiter le correctif de la licence obligatoire; et, subsidiairement, on pourrait tout au moins demander, qu'il soit bien précisé que, celui qui aura fait des propositions raisonnables de licence aux industriels que le brevet peut intéresser, ne pourra jamais être considéré comme n'ayant pas exploité, et qu'il y aura là en tous cas, une justification des causes de son inaction; plus subsidiairement encore, en cas d'opposition intransigeante de l'Angleterre, il faudrait demander tout au moins à la Conférence de dire que l'exploitation dans un pays, quand elle aura vraiment lieu, devra être considérée comme suffisante, non pas quand elle sera principale ou presque principale, mais quand l'importation dans le pays ne l'emportera pas sur la fabrication. Telles étaient les conclusions du rapporteur général, et comme terme à la discussion, le Congrès de Nancy émit le voeu suivant:

"Le Congrès émet à nouveau le voeu que l'obligation d'exploiter soit supprimée dans les rapports internationaux; qu'en tout cas, à la prochaine conférence de révision, l'unification des lois sur cette matière soit obtenue."

---

[1] V. *Bull. de l'Assoc. franç. ind.* déjà cité, N° I, 2° série, p. 16, avec la lettre accompagnant la communication du projet au ministre, le 2 mars 1907.

[2] V. annexe au procès-verbal de la séance du 18 fév. 1909. Projet de loi N° 2320, renvoyé à la Comm. du Commerce et de l'industrie.

[3] Cette Conférence a eu lieu en Mai 1911. Elle a maintenu le système de la déchéance pour défaut d'exploitation.

"Il serait à souhaiter dans ce cas, que l'exploitation dans un des pays de l'Union vaille exploitation dans tous les autres; subsidiairement, que le défaut d'exploitation ne puisse avoir pour sanction que la concession de licence obligatoire, et non la déchéance; qu'en tout cas, la déchéance ne puisse être prononcée lorsque le breveté établira avoir envoyé aux industriels pouvant s'intéresser aux brevets des offres de licence à des conditions raisonnables que ceux-ci n'ont pas agréés."

"Qu'enfin, l'exploitation soit considérée comme suffisante quand le breveté fabriquera dans chaque pays au moins autant d'objets brevetés qu'il en importera dans le pays."

Ce voeu fut renouvelé au Congrès de Bruxelles de 1910, qui chargea l'Association Internationale de l'incorporer dans le projet de réforme présenté à la Conférence de Washington de mai 1911.

Le Bureau International de Berne et le Gouvernement des Etats-Unis, sans accepter intégralement le texte du voeu émis avec tant de persévérance que les Congrès Internationaux proposèrent cependant dans leur avant-projet (art. 7 & 9)[1] de substituer à la vieille règle de l'obligation d'exploiter principalement dans le pays d'origine à peine de déchéance[2] le principe de l'exploitation commerciale avec autorisation de fabriquer dans l'un ou l'autre des pays unionistes ce qui constituait tout au moins un progrès libéral et préparait pour l'avenir la suppression sous condition de l'obligation d'exploiter.

La résistance intransigeante de certains délégués, et notamment des délégués anglais, empêcha la prise en considération du voeu unanime cependant des Congrès Internationaux, et ne rendit même pas possible le vote des propositions du Bureau de Berne (art. 7 & 8). L'art. 5 nouveau de la Convention de Washington maintient la déchéance pour non-exploitation dans le délai de trois ans.[3]

Il est profondément regrettable qu'en dépit de l'opinion unanime des jurisconsultes, ingénieurs et industriels de tous les pays, et malgré les leçons d'une longue expérience, on puisse maintenir une disposition aussi inutile sinon dangereuse que celle de l'obligation d'exploiter, même corrigée par l'autorisation d'introduire de l'étranger unioniste.

---

[1] V. *Bull. de l'Assoc. fr. ind.* déjà cité, N° 5, 2° Série, 1909–1910, p. 129.

[2] Règle absurde d'ailleurs, puisque, dans le cas d'un brevet pris dans divers pays de l'Union, elle est inapplicable; on ne peut en effet exploiter principalement dans plus d'un pays à la fois.

[3] Il convient de remarquer que le texte de la Convention de Washington n'a encore été ratifié par aucun des pays représentés.

On avait cru trouver dans la nécessité de protéger le travail national la raison d'obliger le breveté à exploiter l'invention, dont l'Etat lui garantissait la protection. Malgré la prédominance encore persistante du régime protectionniste, le prétexte, jadis donné pour légitimer l'obligation d'exploiter les brevets, n'est aujourd'hui pris au sérieux par personne, et les arguments qui militent en faveur de la suppression de l'obligation d'exploiter (en dehors même de l'impression que peut causer l'unanimité persistante des Congrès compétents) sont trop connus pour qu'il soit nécessaire d'y insister.

Il apparaît donc bien incontestablement aujourd'hui que l'obligation d'exploiter doive disparaître prochainement des lois sur les brevets d'inventions; toute la question est de savoir si elle doit disparaître sans condition ou avec l'organisation de licences obligatoires. A cet égard, les opinions sont trop contradictoires pour que l'on puisse être aussi absolu qu'au sujet de la suppression du principe même de l'obligation d'exploiter.

Quoiqu'il en soit l'Association Française pour la Protection de la Propriété Industrielle, dans son Assemblée Générale du 17 mai dernier, a approuvé à l'unanimité un rapport de M. Henri Allart, destiné à être présenté au Congrès tenu à Londres du 3 au 8 juin sur l'initiative de l'Association Internationale Industrielle, lequel rapport conclut au maintien intégral des voeux et du projet voté au Congrès de Bruxelles de 1910, et demande à la prochaine Conférence Internationale, qui reprendra les travaux de la Conférence de Washington, de supprimer définitivement l'obligation d'exploiter et de la remplacer par l'institution d'un système de licences obligatoires.

Le Congrès de Londres, à son tour, confirmant les résolutions du Congrès de Bruxelles et le vote de l'Association française, vient d'émettre à l'unanimité le voeu présenté par M. H. Allart.

Devant la persistance des intéressés, particulièrement compétents à réclamer une telle réforme, il y a lieu de croire, que la prochaine Conférence Internationale sera obligée de se prononcer expressément sur une question mûre pour une solution, et qu'à défaut de pouvoir voter un texte formel, elle émettra un voeu caractéristique et préparatoire d'une solution prochaine.

Donc les voeux persistants des Congrès comme les considérations économiques semblent imposer l'institution de licences obligatoires, mais, si l'on examine de près dans quel cas il y aura lieu d'imposer la concession de licences, quelle juridiction les distribuera, dans quelles conditions et à qui seront-elles octroyées, on se heurte à des difficultés pratiques énormes. Aussi a-t-on envisagé un autre système: l'expropriation; mais il n'existe à cet égard aucun projet précis, et, si ce mode de solutionner la question de l'exploitation, dans l'intérêt général, de certains brevets particulièrement utiles, est à priori séduisant, il comporte, en consacrant le principe d'une intervention, selon les cas du pouvoir exécutif, administratif ou judiciaire, un élément de danger pour la liberté commerciale et industrielle. C'est en tous cas une question à examiner de très près et sur le mérite de laquelle on ne pourra se prononcer que lorsqu'on se trouvera en face de textes précis.

La question de la suppression de l'obligation d'exploiter unanimement désirée apparaît donc comme autant justifiée dans son principe que difficilement réalisable dans la pratique; il faudrait d'abord prévoir un mode de licences obligatoires ou d'expropriation pour cause d'utilité publique ou privée, ou tout autre système susceptible d'être accueilli unanimement: c'est sans doute sous l'influence de ces considérations d'intérêt pratique que la Conférence de Washington a maintenu, an quelque sorte, malgré elle, l'obligation d'exploiter les brevets d'invention à peine de déchéance.

BREVET INTERNATIONAL PERMETTANT DE SIMPLIFIER LES CONTESTATIONS ENTRE ETRANGERS

PAR ED. DE LAIRE
*President de la Section Française XI^a^*
Industrielle, Paris, France

En 1909, au VII° Congrès de Chimie Appliquée, à Londres, j'ai émis quelques idées sur la nécessité d'un brevet international destiné à remplacer les brevets nationaux dans les contestations entre étrangers.

En 1910, a Bruxelles, l'Association Internationale pour la protection de la Propriété Industrielle avait inscrit à son programme "L'Unification des Lois sur les brevets d'invention dans chaque pays". Mais cette question ne fut pas traitée: lorsque son tour vint, le Congrès touchait à sa fin et l'assemblée ne paraissait pas préparée à la discuter. Mr. le Pr. Osterrieth exposa donc simplement ce qu'il croyait utile de faire pour réunir les indications et renseignements qui, selon lui, devaient servir de point de départ à une discussion dans un prochain Congrès.

Quelques jours plus tard, Mr. Couhin, Avocat français très distingué, mort malheureusement depuis, fit adopter au 3° Congrès International des Associations d'inventeurs (Bruxelles, Septembre 1910) un voeu tendant, lui aussi, à la création de brevets internationaux.

Cette idée de la simplifications et de l'unification des lois sur les brevets est du reste déjà ancienne. MM. Pouillet, Maillard, Amengaud, et d'autres, en ont parlé en France, à plusieurs reprises; mais ils l'ont fait d'une façon générale, sans entrer dans les détails et en paraissant craindre que le moment ne fût pas encore venu de la proposer à une discussion internationale.

Je crois que Mr. le Pr. Osterrieth était aussi un peu de cette opinion jusqu'à ces derniers temps.

Le programme qu'il a soumis, il y a 2 ans, au Congrès de la Propriété Industrielle à Bruxelles me fait cependant espérer qu'il voudra bien, un jour, consacrer à ce sujet un péu de son activité, de son expérience, et de son autorité. Je dois dire, toutefois, que son programme me semble un peu vaste et que je crains que beaucoup d'années ne se passent encore avant que soit accompli le travail considérable qu'il nécessitera.

Or, ce que je viens faire ici, Messieurs, c'est précisément, vous demander si l'étude de cette question ne pourrait pas aller un peu plus vite, et vous montrer qu'elle n'est pas aussi compliquée qu'on le croit généralement.

D'abord, est-il nécessaire d'envisager, dés maintenant, la réforme générale des lois de chaque pays sur les brevets, et l'adoption par les principaux Etats, d'une seule et même législation?

C'est là un idéal très tentant, et je serais le premier à le défendre si je croyais sa réalisation possible dans un délai suffisamment rapproché.

Malheureusement, les législations des principaux pays sont souvent, en matière de propriété industrielle, si différentes, on peut même dire si contradictoires, qu'il est à craindre qu'on ne puisse, avant longtemps, obtenir leur unification. C'est cette crainte d'entreprendre une chose trop longue et trop difficile qui m'a fait penser à la combinaison que j'ai exposée plusieurs fois déjà, depuis 3 ans, soit dans des Congrès, soit dans des articles de journaux, et que j'appellerai:

"Le brevet pour contestations entre étrangers."

Cette idée ne m'est du reste venue que parce que j'ai, personnellement, beaucoup souffert de l'état de chose actuel; et je m'excuse de me citer moi-même, ici, comme exemple de l'utilité de ce que je demande.

J'ai participé, il y a quelques années à la défense de 2 séries de brevets qui ont donné naissance à de nombreux procès, en France, en Allemagne, Angleterre, Belgique, Etats-Unis. C'était le brevet de l'Ionone (Violette Artificielle) et ceux du Musc Artificiel. Pour le Musc, les procès ont duré un peu moins de 15 ans; mais ceux de l'Ionone ont duré plus longtemps car ils ont continué aux Etats-Unis, alors que les brevets étaient déjà expirés en Europe. Dans toutes ces affaires, nous avons eu gain de cause contre les personnes que nous poursuivions comme contrefacteurs. Mais: tantôt, nous avons dû prouver à nouveau, dans un pays, ce qui l'avait été plusieurs fois déjà dans les autres; tantôt, nous avons dû, pour tenir compte de certaines jurisprudences, changer absolument la forme de notre argumentation. Partout nous avons dû recommencer de nouvelles expertises qui n'étaient que la répétition de celles déjà faites ailleurs.

Au cours de ces 15 années de procès dans 5 pays différents, j'ai été amené à voir combien une simplification de la législation internationale des brevets serait utile aux inventeurs et à ceux qui exploitent des inventions.

Il me semble tout naturel que chaque pays reste maître de faire chez lui ce qu'il croit convenable et il n'est pas nécessaire de demander à un Etat de changer les lois qui régissent ses nationaux dans les contestations qu'ils ont entre eux. Mais le procès fait à l'étranger est une chose qui présente des difficultés pour tout le monde: l'Americain, ou l'Anglais qui viennent plaider en France, les éprouvent aussi bien que l'Allemand qui doit se défendre en Angleterre, ou le Belge, ou le Français qui se présentent devant des juges allemands.

Pourquoi alors ne pas dire "Tout différend entre étrangers, à l'occasion d'un brevet, pourra être porté devant un tribunal international; il suffira pour cela que le breveté, après avoir pris et obtenu son brevet dans son pays, l'ait également obtenu devant le bureau international des brevets."

Le 3° Congrès International des Inventeurs (Bruxelles 1910) disait dans son voeu:

"*Article 1.* Les sujets et citoyens de chacun des pays contractants qui auront régulièrement déposé dans l'un de ces pays une demande de brevet pourront s'assurer, dans les autres pays, la protection éventuelle de l'invention moyennant un 2° dépot au bureau international (à Berne), fait par l'entremise du pays de demande."

Cette formule est bonne et on pourrait, en l'appliquant, arriver à un résultat pratique sans toucher aux diverses législations, qui toutes, en réalité n'ont été faites que pour les différends entre nationaux.

Il suffirait, pour cela, de rédiger un réglement, créer un office et constituer un Tribunal; le tout au point de vus uniquement international des brevets.

S'il était institué (en Suisse, par exemple) un Office chargé de délivrer un brevet qui équivaudrait, pour les différents pays qui seront d'accord sur ce principe, à un brevet ordinaire dans les cas de contestations entre étrangers;

Si les procès entre étrangers se rattachant à ce brevet international, pouvaient être soumis à un Tribunal International (à deux degrès) devant lequel on pourrait plaider en déposant des rapports écrits, signés par les avocats nationaux des parties;

Si surtout, les arrêts de ce Tribunal étaient exécutoires, sans autre formalité, dans tous les pays ayant admis le brevet international;

Alors il ne serait plus exact de dire que le brevet international est rendu impossible par la diversité des législations. Chaque législation pourrait rester maitresse chez elle, et les lois nationales devraient, seules, être invoquées dans les différends entre nationaux; mais rien ne s'opposerait a ce que le brevet international, comme les décisions du tribunal international, aient, dans les contestations entre étrangers, une autorité reconnue par les divers états: et la défense de la propriété de l'invention dans le domaine international, cesserait d'être une chose aussi difficile, lente et coûteuse.

Lorsqu'il est fait un contrat d'affaires entre 2 particuliers habitant des pays différents, il est d'usage de stipuler, qu'en cas de procès, tels arbitres ou tels juges, seront compétents. Il suffirait de procéder de même pour créer le brevet international. Les délégués autorisés de plusieurs nations pourraient décider qu'en cas de différends entre étrangers appartenant à ces divers pays, les affaires devraient être portées devant un tribunal convenu d'avance (Tribunal International), lorsque le propriétaire de l'invention mise en cause par le procès prouverait qu'il est muni d'un titre (brevet international) établissant ses droits, et obligeant celui qui l'invoque à s'en rapporter à un réglement spécial (réglement des brevets internationaux).

Tout cela pourrait donc s'orgaiser sans qu'il soit rien changé à la législation intérieure d'aucun Etat et sans que personne puisse y trouver à redire, puisque la demande d'un brevet international ne serait pas obligatoire, mais facultative pour l'inventeur. Enfin, il n'y aurait pas à craindre que la création de cette organisation internationale change rien au fonctionnement du brevet national propre à chaque pays, dans ce qui concerne son exploitation nationale. Deux nationaux n'auraient pas plus à s'inquiéter dans leurs différends du brevet international, que deux habitants de la même ville ne peuvent aller plaider devant un tribunal autre que celui de leur judiriction naturelle.

J'ai indiqué, dans le rapport qui a été imprimé au Compterendu du Congrès de Bruxelles, les principaux détails de l'organisation de ce bureau international des brevets, je ne les répèterai donc pas ici. Du reste ce ne sont pas les détails qui sont en cause aujourd'hui, mais le principe même de l'institution. Le jour où l'on se décidera à discuter sérieusement cette question, l'organisation sera facile à concevoir. L'important est d'être, d'abord, d'accord sur le principe.

Je montrerai tout—à l'heure, Messieurs, dans un 2° rapport, que la création d'un office International des brevets rendrait de grands services à un autre point de vue, celui de la simplification et unification de l'examen préalable des brevets. Je vous demanderai, après ce 2° rapport, d'émettre un voeu en faveur de l'étude et de la discussion plus approfondie de ces questions, en les fusionnant avec celles du présent rapport.

EXAMEN PREALABLE DES BREVETS

SIMPLIFICATION A APPORTER A SON FONCTIONNEMENT

PAR ED. DE LAIRE

Industriel, Paris, France

La discussion entre partisans et adversaires de l'examen préalable devient chaque jour plus compliquée et ce qui en ressort de plus clair, c'est que personne ne trouve parfait le régime auquel il est soumis.

Les inventeurs font remarquer, en France, que, quand ils veulent vendre une invention on leur demande tout d'abord s'ils ont le brevet allemand ou le brevet américain qui étant soumis à l'examen préalable peuvent seuls donner une garantie du brevet.

Par contre, dans des pays comme l'Allemagne et les Etats-Unis, jusqu'à présent partisans absolus de l'examen préalable, des personnes autorisées commencent à signaler publiquement les inconvénients de la façon dont se fait l'examen officiel. On raconte même que certains employés des bureaux des brevets sont découragés par le nombre toujours croissant des demandes (il y a chaque année plus de 60.000 demandes de brevets aux Etats-Unis), la complication de la littérature scientifique et industrielle, la mauvaise foi et la ruse de certains inventeurs peu scrupuleux.

Avant de rechercher les causes de ces opinions opposées, voyons d'abord ce que désirent avoir les gens de bonne foi lorsqu'ils demandent un brevet sérieux.

Evidemment, ils veulent un titre officiel pour: 1° pouvoir prouver ce qu'était exactement leur invention à une date précise;

2° Pouvoir faire respecter cette invention en s'adressent aux tribunaux lorsque des atteintes sont portées contre elle.

A ces 2 points de vue, l'examen préalable n'est pas indispensable. Par contre, cet examen est évidemment très utile quand on veut montrer à un industriel ou un capitaliste qu'on a une invention ayant de la valeur, ou faire comprendre à des gens trop entreprenants que, s'ils commençaient une contrefaçon, ils devraient courir les risques d'un procés où les chances seraient contre eux.

Mais pour une invention capable de vie et d'avenir, combien y en a-t-il qui disparaissent sans avoir jamais fait l'objet d'aucune tentative d'application! Jusqu'à présent, le législateur considérant que tous les brevets devaient acquitter la même taxe, et étaient, par cela même, égaux devant la Loi, a envisagé de la même façon toutes les demandes.

On peut cependant se demander s'il est utile, pour l'intérêt public, de soumettre à un examen officiel obligatoire un brevet que son propriétaire a pris sans conviction et qui n'intéressera jamais personne. Par contre, on doit désirer que tout brevet sérieux puisse se présenter rapidement devant le public avec un certificat de nouveauté réelle et contrôlée.

Tout industriel qui a exploité des inventions ayant une certaine valeur sait bien qu'une découverte vraie ne peut éviter d'être attaquée qu'à la condition de donner l'impression qu'elle est inattaquable.

Si la discussion ne se fait pas à fond dès la prise du brevet devant un Office officiel, elle sera vite portée devant des juges par des concurrents. De telle sorte que s'il n'y avait que des brevets capables de faire la fortune de ceux qui les exploitent, l'examen obligatoire serait une chose d'utilité indiscutable, et la seule question que l'on aurait à étudier serait celle de savoir comment on pourrait arriver à ce que l'examen du brevet soit le plus rapide, le plus juste et le plus définitif possible.

Mais si l'examen est utile aux inventions sérieuses, peut-on dire que (en dehors de la question d'économie administrative) il y ait des inconvénients à appliquer cet examen indistinctement à toutes les demandes?

Oui; car

1° Cet examen entraine des frais considérables, surtout si on considère que ces frais se renouvellent chaque fois que, pour la même invention, on demande un brevet dans un nouveau pays où existe l'examen préalable légal.

2° Il retarde beaucoup la délivrance du titre officiel. Or, souvent, on ne demande un brevet que pour prendre date et montrer rapidement qu'une route est fermée à recherche de nouveaux arrivants.

3° Avec son organisation actuelle, il est incapable de donner une garantie réelle à personne. Les employés chargés d'examiner les brevets ont souvent trop à faire, ou ne sont pas assez documentés, pour pouvoir poursuivre à fond leur examen. Du reste, ils n'y sont pas obligés; car ils ne sont pas, à proprement parler, responsables des arrêts qu'ils rendent et en réalité ce n'est pas eux, mais les tribunaux, qui tranchent les différends sérieux soulevés par leurs décisions.

Ces différentes considérations m'amènent à vous demander, Messieurs, s'il est vraiment utile que l'examen préalable soit obligatoire pour tous, et s'il faut l'appliquer à ceux qui sont prêts à déclarer qu'ils n'en ont pas besoin?

N'a-t-on pas su tort de concevoir l'organisation actuelle de l'examen préalable comme une règle absolue devant être exactement la même pour tous les brevets; pour ceux qui sont pris hâtivement par des inventeurs peu sérieux et ne seront pas maintenus plus de I an ou deux, comme pour ceux qui n'intéressent personne et ne seront jamais attaqués?

Le bureau officiel des brevets ne devrait-il pas plutôt enregistrer toute demande qui lui est adressée, mais ne soumettre l'invention à l'examen que lorsque l'inventeur le spécifie?

En un mot, ne veudrait-il pas mieux remplacer le brevet actuel par 2 titres:

1° Le brevet comme il existe en France; c'est-à-dire un certificat de dépôt avec prise de date, description de l'invention, etc.

2° Le certificat d'examen, c'est-à-dire la déclaration de nouveauté et, jusqu'à preuve du contraire, de validité de l'invention.

Le brevet devrait-être bon marché, le certificat d'examen pourrait-être plus cher. Si la taxe était beaucoup moins forte lorsqu' il n'y a pas d'examen, cela aurait l'avantage d'aider à ce qu'il se fasse, dès l'origine, une première sélection entre les demandes, et le nombre des inventions soumises à l'examen se trouverait, de cette façon, réduit de beaucoup.

Bien-entendu, la demande d'examen devrait pouvoir se faire aussi bien après la prise du brevet, qu'au moment de son dépôt. Il n'y aurait pas de raison de refuser l'examen à quelqu'un qui ne l'aurait pas sollicité tout d'abord, mais qui, quelques mois plus tard, le trouverait nécessaire à la mise en valeur de son invention.

Il nous semble aussi qu'il faudrait que la demande d'examen puisse être faite par les adversaires du brevet, aussi bien que par le breveté lui-même. Dans ce cas, il parait juste que la taxe soit acquittée par celui qui attaque; mais à la condition qu'elle lui soit, ensuite, remboursée par le propriétaire du brevet, si le brevet était déclaré nul, après révision des objections faites.

On pourrait aussi donner aux examinateurs le droit d'infliger une amende aux personnes qui auraient soumis à leur étude une chose que ces personnes auraient manifestement su ne pas être nouvelle, ou être inexacte.

Un autre perfectionnement auquel on peut aussi penser, c'est celui qui consisterait à faire faire l'examen non pas par un bureau national, mais par un bureau international.

Et ici ma proposition se rattache à celle que j'ai faite précédemment pour le brevet international.

S'il était créé, dans un pays neutre, un comité d'examen des brevets, et si les Etats qui le veulent pouvaient envoyer à ce bureau toutes les demandes pour lesquelles on réclame un certificat d'examen préalable, il y aurait une grande économie de temps et d'argent.

Actuellement, tout brevet sérieux est demandé dans au moins 5 ou 6 pays. Il est donc soumis à plusieurs examens successifs, pendant lesquels le même travail de recherches bibliographiques ou autres, est fait en double ou triple.

Si, d'une part, vous ne soumettiez à l'examen que les demandes qui le désirent; si, d'autre part, cet examen était le même pour tous les brevets de tous les pays qui accepteraient cette combinaison, alors une des grandes objections que certains Etats font contre l'examen préalable disparaitrait.

Lorsqu'une invention a été examinée à fond dans un pays, elle devrait pouvoir être reconnue comme valide par d'autres pays, sans être obligée de subir de nouveaux examens identiques à celui, ou ceux, qu'elle a déja subis.

De plus, les experts officiels, qui auraient fait le Ier examen devraient-être chargés de le compléter lorsque de nouveaux faits seraient opposés au brevet, de telle façon que le travail déja fait soit acquis et puisse être simplement complêté, perfectionné, mais non recommencé continuellement.

Le contrôle des inventions aurait en effet de grands avantages pour l'inventeur, si les difficultés soulevées contre le brevet après sa délivrance pouvaient être soumises au bureau international d'examen au lieu d'être éparpillées, comme elles le sont actuellement, devant une foule de gens différents qui ignorent le travail d'examen déja fait par d'autres avant eux. L'étude de ces faits nouveaux (antériorités, nullités, etc. nouvellement découvertes) serait facile pour des gens connaissant déja à fond la question et ne demanderait, par suite, que peu de temps et peu de frais.

En Résumé

Il semble qu'il y aurait intérêt pour tout le monde à mettre à la disposition de l'inventeur 2 catégories de demandes de brevet:

1° Le brevet simple.

2° Le certificat d'examen; on laissant à l'inventeur le choix de demander le 1er seul, ou les 2 ensemble, ou le brevet d'abord et le certificat plus tard.

On ne peut, dans ce rapport, forcément court, prévoir toutes les questions de détail qui se rattacheraient à cette organisation. Mais tout cela serait facile à régler plus tard en s'inspirant des lois très bien faites qui régissent les brevets dans différents pays. Je dirai simplement qu'il me paraitrait bon de conserver pour la publication des brevets, le secret facultatif d'un an tel qu'il existe actuellement en France.

On pourrait aussi voir si le certificat d'examen ne devrait pas suivant le choix de l'inventeur comprendre soit la simple déclaration du résultat de l'examen, soit l'énumération succincte des recherches faites, et des épreuves et contestations aux quelles aurait été soumis le brevet.—Dans ce cas, ce 2° certificat devrait naturellement faire l'objet d'une taxe plus élevée que celle du premier.

Quand un brevet serait publié, tous ceux qui ont quelque chose à dire contre lui pourraient en référer immédiatement au Bureau des brevets, et le prévenir qu'ils ont une objection à formuler. Cela pourrait être fait soit sous forme d'une espèce de demande en nullité, soit sous toute autre forme, comme cela se passe actuellement avec le Patent Amt ou le Patent Office.

Lorsqu'un brevet est important, il importe pour tout le monde d'être fixé le plus rapidement, le plus sûrement et le plus économiquement possible, sur la valeur qu'il a comme invention nouvelle.

Cela ne peut être fait qu'en provoquant une enquête sérieuse sur tout point douteux se rattachant à cette invention.

Nul ne sera mieux placé, pour procéder à cette étude, que des spécialistes entendant les parties, et faisant, au besoin, contrôler les opinions contraires. Il y a donc lieu de désirer que ce bureau d'examen soit international (c'est-à-dire le même pour les pays qui l'accepteront) et composé de membres appartenant à ces diverses nationalités.

Bien-entendu, les résultats de cet examen sérieux, impartial, contradictoire, devraient pouvoir être soumis à un appel devant un tribunal supérieur international ayant une mission analogue à celle du 1er, mais composé d'autres personnes.

Messieurs, il est bien évident que nos réunions triennales sont trop espacées et trop courtes pour que nous puissions pousser rapidement l'étude de l'idée que je viens de défendre devant vous en vue de la création d'un bureau international de brevets et d'examen des demandes.

Je vous demanderai donc si vous croyez que la discussion approfondie de ces idées soit chose utile de vouloir bien émettre le voeu que:

les associations compétentes (par exemple l'Association pour la Protection Internationale de la Propriété Industrielle) veuillent bien inscrire ces questions au programme de leurs prochaines études, et en saisir, ensuite, s'il y a lieu, les gouvernements intéressés.

EXPERT TESTIMONY

BY EDWARD J. MCDERMOTT
Louisville, Ky.

In answer to the Materialists who said that we know nothing of the soul — that we know only of matter — Bishop Berkeley, two hundred years ago, answered that we know nothing of matter except what God tells us through the senses and the mind; that all our knowledge is due entirely to our mental inferences from experience and thought. It is true that what we ordinarily call "*facts*" are only deductions or inductions from the observations or experiences of ourselves or others. Speaking literally, therefore, all evidence is "opinion evidence"; but speaking practically, all legal evidence, other than the "real evidence" which things themselves afford, may be conveniently divided into (1) evidence of facts by laymen who tell what they have observed in the ordinary transactions of life, and (2) opinion evidence by experts who are persons skilled in matters requiring special or peculiar study or experience.

Neither ordinary witnesses nor experts are allowed to give opinions on matters of common knowledge which jurors may be presumed to understand, and an ordinary witness is generally confined to a statement of facts which he has observed, and will not be permitted to testify to his opinions, inferences or conclusions, based on facts within his knowledge, or based on the testimony of others; and yet the border line between fact and opinion is often very indistinct. Generally, an ordinary witness is allowed to tell only what he has observed, but may sometimes give his opinion as to those facts, appearances and conditions which cannot be satisfactorily described or be otherwise made plain to a jury. It is often hard, if not impossible, for an ordinary witness — from inability to remember all occurrences distinctly, or to describe accurately what he has seen or heard — to tell in detail all the necessary facts to enable an expert witness or a jury to form an opinion on such a statement, and, therefore, the law, from necessity, sometimes allows such an ordinary witness, know-ing the real situation better than it can be described by him, to give his own opinion as to causes, results and conditions.

In the State of Georgia there is a statute which allows an ordinary witness to give his opinion freely, if he can also give the reasons for his opinion. In Utah and Washington it is held that an ordinary witness may give his opinion (1) if he gives his reasons, so that the jury may judge of the value of his opinion; (2) if the subject matter cannot be described precisely as it appeared to the witness at the time; and (3) if the facts are such as men in general are capable of understanding.

In Hardy vs. Merrill 56 N. H. 227 the Court said:

"Opinions of (ordinary) witnesses, derived from observation, are admissible in evidence when, from the nature of the subject under investigation, no better evidence can be obtained."

For this reason ordinary witnesses are allowed to testify to their opinion on the subjects of age, solvency, time, distance, health, size, speed, identity, handwriting and sanity, etc.; but in all such cases the witness must show that his opinion is founded on his personal knowledge, and he is usually required to give the facts and reasons on which his opinion rests. The ordinary witness is not allowed to give his mere conjectures, surmises, suppositions or suspicions. He may describe conduct, demeanor, manner, appearance and looks. He cannot give an opinion as to the probability, possibility or feasibility of an act, cause or result, unless all the facts relating thereto cannot be satisfactorily described to the jurors for their own opinion.

In addition to the ordinary witness, the courts must now and then resort to an expert — to one who, by special study and experience, or by special study alone, or by special experience alone, in some business, profession or calling, or in some matter in which he has had unusual opportunities for knowledge, has acquired more skill or knowledge than ordinary men have, or than a jury or a judge may fairly be presumed to have. The opinion of a carpenter, brick mason, sailor, civil engineer, chemist, physician or surgeon must sometimes be used to aid a jury or judge in determining something concerning his own specialty, and beyond the knowledge or experience of ordinary men. The farmer may smile at the city merchant's ignorance of crops, and the merchant may smile at the farmer's ignorance of the methods of handling commercial affairs. In unfamiliar surroundings or callings, each of us is at times like a fish out of water.

The experts most often used, and of whom there is most complaint at present, are the medical and surgical experts, who testify (1) in criminal trials; (2) in suits for damages for personal injuries; and (3) in will cases where the sanity of a testator is disputed. As such experts are used so much more than all other experts, they may be appropriately treated as a separate class. Unless otherwise indicated, I shall confine my observations to medical, surgical and chemical experts. As the practice and rulings of the various courts in the American States on the subject of experts are not well known to laymen, it may be well to mention briefly the more important rulings in order to see what remedies are needed.

It is for the court, in the exercise of a large judicial discretion, to say whether a man is or is not an expert on any subject, but the court usually passes on the qualifications of the expert perfunctorily, and if the witness has had, or says he has had, any special training or experience, he is usually admitted as an expert, however mediocre or inferior his knowledge or ability. If his opinion is of "some value," though really of little value, the poor jury, with little chance of hastily reaching a just estimate of his ability, must determine the weight of his testimony on the most superficial appearances or statements. He must have had, or say he has had, some special experience, learning or training that would seem to make his knowledge superior to that of an ordinary person, even though he may have long abandoned the practice of his calling. In some States he may be admitted as a professional expert, even though he has never received a diploma from a college, or is not licensed to practise his calling. As a rule, his qualifications are proven only by his own flattering testimony of himself. After he has once been allowed by the court to testify, he cannot be shown by others to be or not to be an expert. A case will not be reversed by a higher court for a mistake in admitting an expert, unless there was a manifest abuse of discretion on the part of the lower court.

Lately, in a court in my city, several medical experts testified in a damage suit that they had removed the female plaintiff's right ovary and part of the left ovary and also the fallopian tubes and that she could never become a mother. Heavy damages for the unhappy plaintiff. That was in March, 1912. But the sad predictions of her physicians were, after the verdict, disproved by REAL evidence — by the birth of a baby — in June, 1912. The indignant defendant naturally wants a new trial.

A doctor when testifying as to personal injuries may relate the clinical history given him by the patient, but, in fact, he generally repeats and seems to confirm the magnified complaints of the patient. In many respects the doctor must rely on the plaintiff for a fair statement of his or her pains, symptoms and ailments. They are usually grossly exaggerated, and yet generally make a deep impression on the jury.

On direct examination, a doctor cannot be asked what the medical books or authorities teach; but, on cross-examination, he may be asked that question to test the accuracy of his knowledge. Books can be referred to in order to contradict what he says is in them, but not to prove a theory contradictory to his. In Davis V. U. S., 165 U. S. 573, it was said that after an expert has expressed his opinion, it is not allowable to interrogate him as to "what other scientific men have said upon such matters, or in respect to the general teachings of science thereon, or to permit books of science to be offered in evidence." In other words, an ignorant doctor or surgeon is fairly well protected from any exposure of his ignorance of the best authorities on the subjects on which he testifies.

It is true that the court allows attorneys to ask an expert questions likely to show his skill, knowledge or experience, and to show what sort of practice he has had, and along what lines his work has been done. He may be required to state the facts on which his opinion is based, and to give the reasons for his opinion. His opinion may be based (1) on his acquaintance with the person or thing under investigation; (2) on a special, medical or surgical examination for the purpose of testifying; and (3) on a hypothetical question in which an attorney is supposed to state the main facts proven by other witnesses, and on which the expert is to give his opinion. When the hypothetical question is asked, only such facts may be stated as the evidence proves or tends to prove; but the questioner need not set out important facts relied upon by his opponent; and yet, the value of the opinion depends mainly upon the completeness and fairness of that statement.

As I have said, expert testimony is absolutely indispensable in many cases, especially where the suit or prosecution involves the subject of murder or personal injury, or sanity. Expert evidence may sometimes show that the testimony of ordinary witnesses is false, and cannot possibly be true; and yet, not only theoretical writers, but the courts themselves, have sometimes strongly condemned the abuses of expert testimony.

In Parker v. Johnson, 25 Ga., 576, Justice McDonald in a dissenting opinion said:

"The rule which admits professional opinions to be received in evidence, a kind of evidence so little reliable, and so fraught with danger to those whose rights and interests it is to affect or control, ought not to be extended."

Justice Daniels said in Templeton v. People, 3 Hun. (N. Y.) 357:

"They (experts) are produced not to swear to facts observed by them, but to express their judgment as to the effect of those detailed by others, and they are selected on account of their ability to express a favorable opinion, which there is great reason to believe, is, in many instances, the result alone of employment and the bias arising out of it. Such evidence should be cautiously accepted as the foundation of a verdict, and it forms a very proper subject for the expression of a reasonable, guarded opinion by the court."

Efforts to regulate expert testimony are generally opposed and obstructed by such lawyers as often appear for defendants in criminal trials, or for plaintiffs in suits for damages for personal injuries; but there are also disinterested lawyers, judges and legal writers who object to proposed statutory reforms on this subject. The unselfish objectors may be divided into two classes:

(1) Those who think that the legal practice now is as good as we can make it, and that any reasonable dissatisfaction is due

to the inefficiency or ignorance of lawyers that examine or cross-examine experts, or to the lack of proper moral or professional standards in the callings of the experts, and that the medical and surgical and other professional societies must simply persuade all their associates to be good; (2) those who think that expert testimony — especially the testimony of medical, surgical or other similar experts — is of very little value anyhow, and is given little weight by juries, and cannot be materially improved by legislation.

These views are inconsistent, and both are unsound. Lawyers are, by habit and training, conservative, many of them too conservative; the law, even in its mere procedure, was changed slowly in England, until 1873, when long needed but radical procedural reforms were happily made. Since then radical but scientific reforms have been made in Germany. Her new codes have been highly praised by great men. In America it seems almost impossible to get us out of the ruinous ruts of a bygone age. Medicine, surgery and chemistry are experimental sciences which have made wonderful progress in the past century, and their students and practitioners in America have far outstripped the lawyers here in meeting the demands of the time. Though a few of our ablest lawyers want a reform of expert testimony to make it more useful in criminal trials, in will cases involving the question of insanity and in suits for damages for personal injuries, the most urgent demands come from the ablest and most scholarly physicians, surgeons and chemists, who chafe under the odium brought on them by the abuses and criticisms due to the present system. It would be absurd to exclude or longer degrade espert testimony in the classes of cases mentioned, and yet that testimony is often ridiculous and sometimes scandalous. It is patent that seemingly respectable, self-styled experts can be gotten for a big fee to testify strongly in favor of almost any extravagant opinion or theory. Errors of judgment or opinion are more likely to occur than errors of observation. Medical or scientific experts do not differ more on the difficult questions of their callings than lawyers and courts differ on hard questions of law; but unless a lawyer is called as an expert witness to prove the law of his State for use in some other State, he does not swear to the correctness of his theories and conclusions. We ought, therefore, to be careful to allow only real experts to testify, and should be more indulgent in our criticisms when they do testify, but the right to cross-examine experts, the indispensable safeguard against falsehood or error, must always be preserved. The lawyer that makes a corrupt use of corrupt expert testimony is as blamable as the experts that help him. The abuse is brought out most plainly in spectacular murder cases, like the cases of Thaw, Haines and Hyde. In all three cases, there has been a miscarriage of justice, for which the courts, the lawyers, the experts and the sensational section of the press were responsible.

THE COURTS SHOULD HAVE MORE CONTROL OVER THE SELECTION OF EXPERTS

A partisan witness is a bad witness who generally cannot or will not tell the plain truth. A party to a suit is allowed to pick his ordinary witnesses, though biased; but usually his range of selection is necessarily limited, because few have seen or heard or know the facts involved. The courts cannot undertake the burden of selecting such witnesses. That must be left to the industrious litigants concerned. In selecting expert witnesses, the litigant has a much wider range of selection. He can pick and test one expert after another, until he finds one who will, for a big fee, swear just what is wanted, and will become a zealous partisan. A court or jury should always prefer an unbiased, non-partisan witness, as everybody prefers an unbiased juror, or an unbiased judge. When only biased witnesses appear, the facts are distorted or suppressed, and a judge or jury can only give a hap-hazard guess at the truth.

Ordinary witnesses, however partisan, are to some extent held in check by the dread of public condemnation, and by the fear of being punished for perjury. An expert witness, when he is only giving his opinion, is practically free from any fear of punishment for perjury, and known that the public cannot well understand, or confidently criticize, his professional theories. There is usually not much ground for complaint when an expert merely proves the settled axions or principles, or even probable theories of his science; but when he begins to apply those theories, for a fee, to a particular case, the glaring evils of partisanship appear. Cæsar said: "Omnes homines fere libenter id quod volunt, credunt." The Germans say: "Man glaubt leicht was man wünscht."

Perjury is far more frequent than the average man believes. If ordinary witnesses — who are allowed only a petty, fixed sum for their attendance in court, who only swear to what they are supposed to have seen with their own eyes, or heard with their own ears, and who will be confronted by actual observers of the same facts — if these ordinary witnesses will swear falsely in spite of the law and its penalties, and public opinion, how much greater is the danger of false testimony from expert witnesses who are paid large sums of money to make their theories fit the needs of their employer, as Procrustes tortured or mangled his victims to make them fit his iron bed. The large compensation of such witnesses is often contingent upon the success of their efforts to manufacture a special scientific theory for that case; and, while they are spinning fine theories and expressing false but plausible opinions, they are practically free from any danger of legal punishment for perjury.

Generally a long list of jurors are selected each term or year by the courts without reference to any particular case. A judge is appointed or elected for a long time, and will try many cases. Hence, any litigant has a reasonable chance of having an unbiased judge and unbiased jurors to try his case. An expert witness is often allowed to express an opinion on the very question which the judge or jury must try. To some extent, such opinion-witnesses are themselves performing the functions of a judge or jury. They ought not to be hired partisans with a contingent or tempting fee. As their opinions may sometimes have almost a controlling weight with a jury, especially in criminal cases, in will contests, and in speculative damage suits involving personal injuries, they ought generally to be selected, like jurors, from lists carefully prepared by the courts long in advance for the trial of cases generally, not selected as partisans for a specific case.

A list of experts should be made up by each Court from the most honorable and most competent men within its jurisdiction, after consultation with such eminent men of the profession as would be able to know who were real experts. They should then, after having had a reasonable opportunity to examine the question, person or thing under investigation, testify in Court and be subject to cross-examination under the careful control of the Court in order to protect them from indignity or badgering, and, as far as possible, to protect the jury from imposition, or plausible pretenses, or gross exaggerations, or personal, extravagant theories.

It is said that the best experts would probably not act as witnesses for the scant compensation likely to be allowed by the court. The court could compel them to serve, but most experts would be willing to serve for the sake of truth, and for the sake of their calling. Many people must serve in office for a compensation far below what they could make in private business. Under existing conditions, a real expert dislikes to be put forward in competition with the charlatan, or a dishonest member of the profession, before a jury that cannot easily discriminate. It is said that the judge cannot be assumed to have special knowledge of the qualifications of experts. It surely may be assumed that men intelligent enough, and well enough acquainted in the community, to become judges, will, at their leisure, and with outside advice, be more likely than a jury to discover who are genuine experts. A judge may, from time to time, hear different experts as witnesses, and may learn of their work and reputation from others, and so may form a fair estimate of their qualifications; but the jury, in the hurry and excitement of a trial, with no previous knowledge of the men, and with no disinterested advice, are compelled to decide quickly on the merits of the conflicting experts, and on the weight to be given them respectively. It is no wonder that they are often deceived. When insanity or a hidden internal injury is feigned by a party, or when the condition or behavior of a dead testator is unintentionally or purposely misrepresented, and when some shrewd but unqualified or dishonest physician or surgeon has spun nice theories and given plausible reasons for his opinion, it is not surprising that a jury, ignorant of his nature and qualifications, may give him more weight than they give to a superior exper of a different opinion.

It may be well to allow parties interested in a legal controversy to have the right to summon experts in addition to those taken from the court's list; but, if that be allowed, then, to prevent surprise to the other side, the party callng them should be compelled to state to the court, before the trial, who his experts are, and where they live, and to state briefly what is to be the general nature of their testimony. With such notice, the opposite party can be prepared to meet incompetent or untrustworthy experts, and their false or doubtful, though plausible, theories. In olden times the court did not try to prevent a meritorious litigant from being beaten by a mere surprise; but the legislatures and the courts now try to prevent such an undeserved overthrow by a surprise. If truth or justice is to be our aim, no advantage should be allowed to unnecessary concealments or mere tricks.

It is also said that, if a list of eligible men be appointed by the court, and that if the parties, nevertheless, be allowed to call their own experts, the parties will continue to select only their own partisan experts. Not when it is observed by lawyers, as it will be, that juries will not give to unaccredited experts, selected and paid by a party for partisan testimony, as much attention or weight as is given to experts long before approved by the court without reference to the controversy on trial. The difference will be apparent to the jury. If the question be so clear that all the impartial experts on the court's list are against one of the parties in the legal controversy, he ought not to be heard to complain. If the question be doubtful or complicated, experts on the court's list will differ. It is said that no distinction, in the selection or in the method of compensation, should be made between medical and other similar experts, and ordinary witnesses and ordinary experts; and yet we are also told (as experience tells us), that medical and scientific experts are needed far oftener than all other professional experts put together. Here is a valid reason for a difference of treatment.

Wherever experts are to testify as to any living person or existing thing, there should always be afforded to the experts a reasonable opportunity to study the question involved, and to examine the person or thing under investigation. If a living man's sanity is being considered, the experts should have a chance to watch him in a suitable place when he is not conscious of being observed. In my city a few years ago, a man who claimed to be seriously and permanently injured in an accident, said he could not stand erect, and maintained a stooping posture for several years; and, while his case was in the Court of Appeals, he was observed one day to straighten himself up unconsciously when the horse in his wagon started to run away, while the plaintiff was standing on the sidewalk. Unmindful for the moment of his lawsuit, he ran and overtook the horse, and stopped him, before remembering that he had long pretended that he was unable to straighten himself up, or to walk with ease. When his attorney learned that this strange occurrence had been observed by several witnesses, the case was compromised. In St. Louis, the jail physician, and several other physicians who voluntarily aided him, have made it a rule to secretly watch prisoners who plead insanity to escape the punishment of a crime. In that way, the mental unsoundness of several prisoners was made apparent, and the shamming of others was easily detected.

The courts in this country have generally held that the legislature has general power to regulate evidence, subject only to a few constitutional limitations. The legislature and the courts can, and in some respects do, limit the number of witnesses allowed on questions before a jury. In order to protect a poor litigant from being overwhelmed by the money of a rich opponent, and in order to prevent a criminal trial from being unduly protracted and made farcical by the great number of experts called by rich criminals, the number of experts ought to be limited by statute, or by judicial regulations.

Under no circumstances should an expert be allowed to have a contingent fee. It ought not to be possible for an expert to have a secret monetary interest in the result of his testimony. Temptation to commit perjury is thus made too strong for ordinary men. In the words of the great prayer we cannot too often repeat: "Et ne nos inducas in tentationem." In all cases the compensation of an expert, whether called from the list of the court or selected by the parties alone, should be controlled by the court, and the expert should be criminally punished if he attempts to collect, or contracts for, any compensation other than that allowed by the court or the statutes. I once saw, by accident, the private ledger of a physician who frequently appeared as an expert witness in court, and his books showed that in cases in which he testified, he got no fee if his employer lost, and he got a big percentage of the amount recovered in case of victory. Such a practice must produce perjury and corruption.

The whole world is interested in this topic. Whenever Courts administer justice — one of the foremost objects of every civilized state — there must be an effort to improve legal procedure and so to regulate trials as to save costs and time and to avoid any technicalities or tricks or false testimony that may prevent a right decision or bring about a miscarriage of justice.

DE LA BREVETABILITE DES PRODUITS PHARMACEUTIQUES

PAR A. TAILLEFER

Docteur en Droit, Avocat à la Cour d'Appel de Paris, Ancien Elève de l'Ecole Polytechnique. Secrètarie-General de l'Association Française pour la Protection da la Propriété Industrielle.
Paris, France

La plupart des Lois prohibent, en dehors des inventions contraires au bonnes moeurs et à l'ordre public, la brevetabilité des compositions pharmaceutiques, des remèdes et médicaments, et aussi parfois des produits alimentaires et des produits chimiques. C'est ainsi que les médicaments ne peuvent être brevetés en Allemagne, dans la République Argentine, en Autriche, (y compris les désinfectants) en Belgique, Danemark, Espagne, France, Hongrie, Italie, Japon, Norvège, Portugal, Roumanie, Russie (y compris les procédés pour les obtenir) Suède, Suisse Tunisie, etc.

Cette exception est étendue aux produits alimentaires par les Lois d'Allemagne, d'Autriche (exclusivement pour les produits alimentaires destinés à l'homme) Danemark, (y compris les procédés) Hongrie, Japon, Norvège, Roumanie, Russie, (y compris les procédés) Suède, Suisse, etc. Enfin, la brevetabilité est refusée aux produits chimiques, indépendamment des procédés de préparation par l'Allemagne, l'Autriche, la Hongrie, le Mexique, le Portugal, la Russie (y compris les procédés) la Suède, la Suisse, etc.

Aux Etats-Unis, il ne semble pas qu'il existe de restrictions de cette nature. On justifie l'exclusion de la brevetabilité des compositions pharmaceutiques et des remèdes, par la crainte qu'en pareille matière, le brevet devienne une arme entre les mains de charlatans, et aussi qu'un inventeur ne puisse de la sorte accaparer un remède nouveau en spéculant sur la santé publique.

Des raisons analogues sont mises en avant pour justifier l'exclusion de la brevetabilité des produits alimentaires; quant aux produits chimiques, les législations qui les excluent estiment que autoriser la brevetabilité des produits chimiques en dehors des procédés de fabrication, c'est risquer de paralyser l'industrie et la condamner à la stagnation; lorsqu'un produit étant breveté comme tel, un tiers découvre presque tout de suite après la prise du brevet, un procédé de préparation beaucoup plus simple, plus pratique, et plus économique.

Certaines personnes ont cru voir, dans cette particularité de la Loi Allemande notamment, l'une des causes du grand développement de l'industrie chimique dans ce pays.

On peut se demander si les diverses raisons invoquées pour justifier les restrictions de la brevetabilité sont fondées; il est permis de penser le contraire, spécialement l'argument invoqué pour exclure de la brevetabilité les produits pharmaceutiques consistant à vouloir empêcher un inventeur de monopoliser abusivement entre ses mains des médicaments essentiels à l'humanité, parait quelque peu puéril.

D'abord, malheureusement, les médicaments d'utilité et d'efficacité primordiale sont encore à trouver, et en tous cas très rares, et viendraient-ils à être découverts, il est tellement de l'intérêt de l'inventeur d'exploiter une pareille découverte et de la mettre par conséquent à la disposition des consommateurs, qu'il n'y aurait guère lieu de craindre qu'il en réservât le bénéfice aux seuls privilégiés de la fortune. D'autre part, on peut remarquer que ces restrictions sont la source de difficultés et d'incertitude, et surtout n'ont qu'une efficacité restreinte. En France par exemple, où la Loi exclut les compositions pharmaceutiques et les remèdes considérés comme tels, en laissant le droit de brevetér les procédés de fabrication, souvent la brevetabilité du procédé assure indirectement le monopole du produit si ce procédé est unique. Il faudrait alors interdire même la brevetabilité du procédé qui peut être général et utile pour l'obtention d'autres produits non médicinaux.

D'autre part, la Loi Française autorisant la prise d'un brevet pour les produits chimiques, il suffit, lorsque le remède, comme cela a lieu dans la plupart des cas, est un produit chimique susceptible d'applications industrielles, de prendre le brevet pour le produit chimique en ayant bien soin de passer sous silence les applications thérapeutiques: dans ces conditions, l'Administration se trouve désarmée et le brevet est délivré.

Il semble que la solution de beaucoup la plus sage serait de faire disparaitre tous ces obstacles qui se dressent devant l'inventeur et d'admettre la brevetabilité de tout ce qui peut constituer une invention, sauf, le cas échéant, s'il apparaissait que l'invention a une portée spéciale d'utilité générale, à lui appliquer les règles qui existent dans la plupart des pays pour l'expropriation pour cause d'utilité publique et à donner au Gouvernement le droit d'exproprier l'invention.

Dans beaucoup de législations, et c'est là encore une exception qui aurait dû s'ajouter aux autres énumérées plus haut, une situation spéciale est faite aux inventions intéressant la défense nationale, les Administrations sont autorisées à ne pas délivrer de brevets pris pour de telles inventions, et l'Etat s'arroge le droit de s'en emparer moyennant indemnité. La plupart du temps, cette indemnité est fixée de gré à gré entre l'Etat et l'inventeur; faute d'entente, elle est déterminée par arbitres.

Il suffirait de généraliser ces principes et d'organiser dans les différents pays une procédure générale d'expropriation pour cause d'utilité publique pour qu'immédiatement et sans le moindre inconvénient, toutes les exceptions à la brevetabilité inscrites dans les diverses Lois puissent disparaître.

Ce serait là une simplification et aussi une oeuvre de justice; il n'est pas juste en soi qu'une catégorie d'inventeurs, se livrant à des travaux essentiellement utiles, se trouvent, par la nature même de ces travaux, exclus du droit d'obtenir, par la prise d'un brevet, la juste récompense de leurs peines.

Le Congrès pourrait émettre le voeu de voir disparaitre des Lois nationales les différentes restrictions apportées à la brevetabilité, notamment en matière de produits pharmaceutiques, sous réserves d'organiser avec des garanties suffisantes pour les inventeurs, une procédure générale d'expropriation des brevets.

DE L'UTILITE D'UN ENREGISTREMENT INTERNATIONAL DE PLIS CACHETES

PAR ANDRE TAILLEFER
Avocat à la Cour de Paris, Docteur en Droit, Ancien élève de l'Ecole Polytechnique
Secrétaire général de l'Association Française pour la protection de la Propriété Industrielle

L'utilité pour les créateurs de la pensée, quels qu'ils soient, d'avoir à leur disposition un moyen simple d'assurer une date certaine à leurs idées ne saurait être discutée.

L'industrie est soumise à des transformations incessantes. Les inventions se succèdent tous les jours, et il n'est guère possible de breveter tout ce qui s'y fait de nouveau. La prise d'un brevet entraine des frais relativement considérables, et a en outre le défaut de révéler à tous l'invention qui en est l'objet. Par contre, il est fort utile de pouvoir se réserver le moyen d'établir de façon non contestable que tel perfectionnement ou tel procédé a été imaginé à un jour déterminé.

Cette précaution est indispenésable pour pouvoir, le cas échéant, invoquer contre un tiers qui réaliserait la même invention et la breveterait, le droit de possession personnelle et même si un brevet doit être pris, elle reste utile pour se préserver contre les usurpations qui peuvent provenir de tiers appelés à un titre quelconque à participer à la mise au point de l'invention avant le moment où elle peut être brevétée.

De même, et peut-être encore plus, celui qui crée des dessins ou des modèles, et qui, pour l'exécution matérielle de ses objets, a presque toujours besoin de recourir à de nombreux intermédiaires spécialistes, risque fort d'être dépouillé de ses droits s'il n'a à sa disposition un moyen facile et peu coûteux de prendre date et d'établir l'époque à laquelle est née la conception qui n'a pu être matériellement réalisée que plus tard. De même encore, le savant qui fait une découverte dans son laboratoire, même s'il n'entend pas en tirer un profit pécuniaire, peut du moins prétendre ne pas être dépouillé de la gloire d'être le premier à l'avoir faite, et a lui aussi, intérêt à pouvoir en fixer la date.

L'avantage est le même pour le littérateur qui concoit le titre d'un ouvrage et en règle dans son esprit les scènes principales avant de lui donner la forme définitive.

Comment la date de ces créations peut-être être prouvée?

Le procédé usité qui varie suivant les législations et les habitudes des différents pays, est le dépôt de plis cachetés dans les Archives, soit de notaires publics, soit de Sociétés scienfifiques ou industrielles, ou quelquefois encore l'enregistrement fiscal d'un document comportant une description de l'invention ou de la création; ces moyens assurément utiles comme preuves de droit commun manquent tous plus ou moins de certitude et peuvent être discutés. Il y aurait grand intérêt à les perfectionner.

L'association Française pour la protection de la propriété industrielle s'est, à l'instigation de son Président Mr. Soleau, préoccupée de cette question depuis longtemps, et elle propose à cet effet l'emploi de deux enveloppes géminées contenant chacune un exemplaire identique du document dont l'inventeur désire établir la priorité. Ces enveloppes comportent des ouvertures analogues à celles que présentent certaines enveloppes destinées spécialement à l'envoi des cartes postales, et permettant l'apposition du titre d'affranchissement sur le document même, et aussi, par suite, des cachets d'oblitération postale. Ces enveloppes seraient envoyées à une administration d'Etat; les Offices nationaux de propriété industrielle dans les différents pays paraissent tout indiqués à cet effet.

A leur arrivée, elles seraient revêtues d'un numéro, répertoriées sur un registre, et perforées à la date et à l'heure de leur arrivée.

L'un des exemplaires serait conservé par l'établissement et l'autre renvoyé l'inventeur qui aurait ainsi entre les mains une preuve dont l'importance pour lui n'a pas besoin d'être soulignée. La perforation, si elle couvre toute la surface du document a pour effet si l'on proscrit l'usage de l'impression, de rendre pratiquement impossible toute modification ultérieure à ce document; les modifications ou additions apparaissant à un examen tant soit peu attentif.

Si, en outre, cet envoyeur prenait soin de copier au copie-lettres le document mis sous enveloppe avante de l'envoyer, il semblerait très difficile, lorsque la teneur du document et celle du copie de lettres seront concordantes de texte, d'en discuter la date.

La plupart du temps, cet enregistrement national serait pour lui suffisant, mais on conçoit que le moyen proposé se prête immédiatement à un enregistrement international; il suffirait que l'établissement récepteur, au; lieu de garder l'une des enveloppes géminées, après avoir envoyé l'autre à l'expéditeur, et expédié l'enveloppe gardée à un établissement choisi ayant un caractère international, ce pourrait être par exemple, le Bureau de la Propriété intellectuelle à Berne, qui, si nous sommes bien renseignés, serait tout disposé à accepter cette tâche.

Cette enveloppe subirait à son arrivée à Berne un enregistrement à un répertoire, serait classée dans les archives et deviendrait ainsi un titre irréfragable en faveur de l'envoyeur. Les établissements chargés de recevoir, conserver et réexpédier les plis cachetés, seraient rémunérés au moyen de timbres spéciaux, émis par eux, qu'il serait facile à tous de se procurer et qui seraient apposés au verso du pli à eux expédié. Ces timbres seraient détachés et détruits par chaque établissement lors de la réception de l'envoi.

Tel est, dans ses grandes lignes, le procédé imaginé par l'Association Française pour la protection de la propriété industrielle, et qui parait à la veille d'entrer dans la pratique en France.

Si le Congrès estime qu'un tel procédé soit de nature, et ceci parait difficilement contestable, à rendre service aux divers créateurs de la pensée, il pourrait émettre un voeu en faveur de son adoption par les différents Etats.

Ce voeu pourrait être ainsi formule:

"Le Congrès estime que le système d'enregistrement national et international d'enveloppes proposé par l'Association Française pour la protection de la propriété industrielle, serait de nature à rendre les plus grands services à tous les créateurs de la pensée et émet le voeu que ce système soit adopté, tant au point de vue national qu'au point de vue international, par les différents Etats."

GENERAL INDEX
TO THE TWENTY-FOUR VOLUMES OF ORIGINAL COMMUNICATIONS

Volume	Section	
1	I.	Analytical Chemistry.
2	II	Inorganic Chemistry.
3	IIIa	Metallurgy and Mining.
4	IIIb	Explosives.
5	IIIc	Silicate Industries.
6	IV	Organic Chemistry.
7	IVa	Coal Tar Colors and Dyestuffs.
8	Va	Industry and Chemistry of Sugar.
9	Vb	India Rubber and other Plastics.
10	Vc	Fuels and Asphalt.
11	Vd	Fats, Fatty Oils and Soaps.
12	Ve	Paints, Drying Oils and Varnishes.
13	VIa	Starch, Cellulose and Paper.
14	VIb	Fermentation.
15	VII	Agricultural Chemistry.
16	VIIIa	Hygiene.
17	VIIIb	Pharmaceutical Chemistry.
18	VIIIc	Bromatology.
19	VIIId	Biochemistry including Pharmacology.
20	IX	Photochemistry.
21	Xa	Electrochemistry.
22	Xb	Physical Chemistry.
23	XIa	Law and Legislation Affecting Chemical Industry.
24	XIb	Political Economy and Conservation of Natural Resources.

ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS
OF APPLIED CHEMISTRY

Washington and New York

September 4 to 13, 1912

SECTION XIb: POLITICAL ECONOMY
AND CONSERVATION OF NATURAL RESOURCES

VOL. XXIV

ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

CONGRESS OF APPLIED CHEMISTRY

Washington and New York

September 4 to 13, 1912

SECTION XIb: POLITICAL ECONOMY AND CONSERVATION OF NATURAL RESOURCES

VOL. XXIV

The matter contained in this volume is printed in exact accordance with the manuscript submitted, as provided for in the rules governing papers and publications.

La matière de ce volume a été imprimée strictement d'accord avec le manuscrit fourni et les règles gouvernant tous les documents et publications.

Die in diesem Heft enthaltenen Beiträge sind genau in Übereinstimmung mit den uns unterbreiteten Manuskripten gedruckt, in Gemässheit der für Beiträge und Verlagsartikel geltenden Bestimmungen.

La materia di questo volume e stampata in accordo al manoscritto presentato ed in base alle regole que governano i documenti e le publicazioni.

THE RUMFORD PRESS
CONCORD·N·H·U·S·A·

ORIGINAL COMMUNICATIONS

TO THE

EIGHTH INTERNATIONAL CONGRESS

OF

APPLIED CHEMISTRY

APPROVED

BY THE

COMMITTEE ON PAPERS AND PUBLICATIONS

IRVING W. FAY, CHAIRMAN

T. LYNTON BRIGGS
JOHN C. OLSEN
F. W. FRERICHS
JOSEPH W. RICHARDS
A. C. LANGMUIR
E. F. ROEBER
A. F. SEEKER

SECTION XIb. POLITICAL ECONOMY AND CONSERVATION OF NATURAL RESOURCES.

Executive Committee.

President: J. A. Holmes, Sc.D., LL.D.
Vice-President: C. R. Van Hise, Ph.D., LL.D.
Secretary: Charles A. Davis, Ph.D.
Gifford Pinchot, Sc.D., LL.D.
Emory R. Johnson, Ph.D.

Sectional Committee.

L. H. Bailey, LL.D.	Cyril G. Hopkins, Ph.D.
John R. Freeman, Sc.D.	C. Hart Merriam
John Hays Hammond, LL.D.	L. B. Stillwell, Sc.D.

and the Sectional Executive Committee.

VOLUME XXIV

SECTION XIb: POLITICAL ECONOMY AND CONSERVATION OF NATURAL RESOURCES

CONTENTS

PAGE

BAIN, J. WATSON
The Chemical Industries of Canada 7

BIRKENBINE, JOHN
Synopsis 45

CARVER, T. N.
What the States are Doing Toward the Conservation and Improvement of Soil Fertility 47

CONNER, ELI T. (see GRIFFITH, WILLIAM)

COTTRELL, F. G.
The Research Corporation, an Experiment in Public Administration of Patent Rights 59

GRAVES, HENRY S.
What the Government is Doing in Forestry 71

GRIFFITH, E. M. (see VAN HISE, CHARLES R.)

GRIFFITH, WILLIAM AND CONNER, ELI T.
Our Anthracite Coal Supply and its Conservation 79

HAZEN, ALLEN
Progress in Developing and Conserving Water Supply for Municipal and Domestic Purposes 115

NEWELL, F. H.
Conservation and Use of Waters in the Reclamation of Arid Lands Through Governmental Agencies 131

ROBINSON, J. ALBERT
The Relation of the Chemical Industry to the Annual Fire Loss of the United States 143

VAN HISE, CHARLES R. AND GRIFFITH, E. M.
The Conservation Movement in Wisconsin 181

THE CHEMICAL INDUSTRIES OF CANADA

J. Watson Bain

Introduction

The manufacture of chemical products occupies a late chapter in the history of the industrial development of a state. Not until the arts have made very substantial progress does there arise a demand, either for those materials which it is the province of the chemist to supply, or for the assistance which he can offer towards the improvement and control of manufacturing processes. The capitalist who studies the growth of industry in a young country, perceives that there is only a small market for chemical products, that the equipment and some, at least, of the raw materials are costly, and that labor is dear; and concludes that another form of investment is preferable.

With a powerful and prosperous nation to the south, highly skilled in manufacturing processes and seeking eagerly for markets for its surplus production, Canada has developed more slowly from an industrial point of view than if she occupied a more isolated position geographically. The products of Europe and of the United States have long been familiar to the Canadian people, and the manufacturers of British North America have had a difficult struggle to establish the good name of their wares. But this day is past. All over the Dominion new factories are building, new articles are being manufactured and new plans for the future are being evolved.

Under conditions such as these, it may readily be understood that until comparatively recently, chemical industry in Canada was of very minor importance. The situation today can only be conveyed with the help of statistics, and the following paper embodies the efforts which have been made by the Canadian Section of the Society of Chemical Industry to place before the Congress a survey of the conditions of the present.

In the preparation of this report, the various manufacturers throughout the country were asked to supply the information desired, and the Canadian Section of the Society of Chemical Industry desire to express their appreciation of the kindly manner in which their requests were answered. In some instances, the manufacturers felt that for business reasons, they could not furnish the data in question, and in such cases, the deficiency has been met by consulting the latest trade or government reports, or by estimates furnished by individuals whose business affiliations lend a high degree of probability to their figures. It must not, therefore, be considered that the statistics herewith presented have the authority of a census return; they are as accurate as it has been possible to make them, and may be accepted as very close approximation to the true figures, which only a government can supply.

Within the confines of the Dominion is to be found a plentiful supply of most of the raw materials of the chemical industry. On the eastern and western coasts and in the Rocky Mountains, excellent coal is at hand; the provinces of Ontario and Quebec have unfortunately no stores of this most valuable mineral. Water power is abundant in all districts, and an electrochemical industry is growing rapidly in the vicinity of the larger water falls. To discuss these various points is the function of the following pages, and this may now be commenced without further preliminaries.

PRODUCTS OF WOOD DISTILLATION

The destructive distillation of wood flourishes in certain parts of Canada where there is an abundant supply of hard wood, maple and beech being preferred. The wood is charred in long horizontal retorts holding six cords each, as is usual in American practice. The crude pyroligneous acid is distilled to remove the tar, the distillate is then treated with lime and redistilled, yielding alcohol, acetone, etc., and a solution of calcium acetate. The alcoholic distillate is fractionated, and is then shipped to the central refinery for a further rectification. Some of the alcohol is oxidized to formaldehyde, for which there is a considerable demand. A portion of the calcium acetate is used in the manufacture of acetone, which is marketed in England for the smokeless powder industry.

Four companies are engaged in this branch of manufacturing. The oldest and largest of these is the Standard Chemical Iron and Lumber Co., Ltd., head office at Toronto, which operates plants at Sault Ste. Marie, South River, Longford and Parry Sound in Ontario; and at Fassett, Cookshire and Mont Tremblant in Quebec. This company has a refinery in Montreal and treats the output of all the other producers; acetone and formaldehyde are likewise manufactured. In order to utilize the surplus charcoal, the Company runs a charcoal iron furnace at Deseronto, Ont. The Wood Products Co. of Canada, Ltd., head office at Toronto, has a plant at Donald, Ontario; and the Thornbury Reduction and Transportation Co., Ltd., head office at Thornbury, Ont., have just commenced operations. The Dominion Chemical Co., Ltd., head office at Weedon, Que., have been carrying on the distillation of wood for the past two years.

These companies have an aggregate capital of $5,965,000, and employ about 2300 men. The amount and value of each of the products in the aggregate is given below:

Charcoal	8,000,000 bushels of 20 lb.	$560,000
Acetate of Lime	14,000 tons	465,000
Wood alcohol	1,019,000 Imperial gals.	489,000
Acetone	400 tons	110,000
Formaldehyde	1,400 barrels	50,000
		$1,674,000
Pig Iron	18,000 tons	325,000
		$1,999,000

PRODUCTS OF WOOD DISTILLATION

Plants

Standard Chemical Iron & Lumber Co.

Ontario—Sault Ste. Marie	112	cords
South River	48	"
Longford	48	"
Parry Sound	48	"

Quebec—Fasset	36 "
Cookshire	48 "
Mont Tremblant	36 "
Wood Products Co.	
Donald, Ontario	48 cords
Thornbury Reduction Co.	
Thornbury, Ontario	24 cords
Dominion Chemical Co.	
Weedon, Quebec	24 cords

Products of Coal Tar Distillation

In connection with gas works and coke ovens, tar and sulphate of ammonia are being produced at a number of points as specified below; a number of smaller producers have made no returns.

Until five years ago, no coal tar was distilled in Canada for lack of market. No dyestuffs are manufactured in the Dominion, and in consequence the products of tar distillation have to be exported except for small quantities for domestic use. The creosote oils have found extended employment in the United States for the preservation of timber, and large quantities have been imported annually from Great Britain. The corresponding demand in Candaa is being met by home manufacturers and a development of the industry is for this and other reasons, quite probable.

Five companies are engaged in this branch of chemical manufacture. The Canadian Ammonia Co., capital $250,000, head office at Detroit, Michigan, has a plant in Toronto in connection with the Consumers' Gas Co., and produces ammonia in its various forms. The Dominion Tar & Ammonia Co., Ltd., capital $25,000, head office at Hamilton, Ont., operate in connection with the Hamilton Gas Co., and produce ammonia as well as the various tar distillates. The Algoma Steel Co., Ltd., head office and works at Sault Ste. Marie, Ontario, operates two batteries of 55 ovens each, of the Kopper type. Each charge is 12¾ tons of coal, and the gas is cooled, filtered, superheated and passed through sulphuric acid in Wilton saturators; the plant was started in March, 1911. The Dominion Iron and Steel Co., Ltd., capital $25,000,000, head office and works at Sydney, Nova Scotia, also carries on the coking of coal mined by a subsidiary company, the Dominion Coal Co., Ltd. Ammonium sulphate is produced in considerable quantity, and the tar is sold to the Dominion Tar and Chemical Company, Ltd., head office at London, Eng., who have their works on the property of the Dominion Steel Co. By distillation are produced the following products: refined tar, soft pitch, briquetting pitch, black varnish, roofing cement, soluble disinfectant or sheep dip, crude benzole, rectified benzole, creosote oil, liquid creosote, creosote stain, crude carbolic acid, purified carbolic acid, crude naptha, purified naptha, emulsion (germicidal), ammoniacal liquor and light oil.

At these plants a total of 706,700 tons of coke, 7100 tons of ammonium sulphate and about 5,000,000,000 gallons of tar are produced. The value of these is approximately $4,600,000.

FERTILIZERS

The use of commercial fertilizers in Canada has scarcely passed the infantile stage, although in the Maritime provinces, more especially in the fruit and potato-growing districts, fertilizers have been popular for years. Ontario and Quebec have, during the past five years, been giving the subject more attention and may be expected to rapidly increase their consumption from this stage.

British Columbia quickly learned the value of fertilizers and takes high rank as a consumer. This year a Victoria firm shipped a carload of fertilizer to Dawson City in the Yukon.

The provinces of the middle-west will not be heavy consumers for many years to come, although the use of fertilizers there has commenced, chiefly among market gardeners and potato growers, but they are also being used to a small extent by grain growers. The prevailing high freight rates necessarily add greatly to the cost of the fertilizer and this aggravates the difficulties of pioneer work.

In the younger provinces of Alberta and Saskatchewan, the interest in the fertilizer question seems greater than in Manitoba. This may be explained by the fact that within recent years there has been a very large emigration of United States and European farmers to Alberta and Saskatchewan, men who already were familiar with the use of fertilizers.

The following table shows the principal fertilizer materials imported into Canada during the years ending June 30th, 1904, and February 29th, 1912, respectively, and a comparison of the two years indicates the increase which has taken place in the intervening period:

	12 Months ending June 30, 1904		12 Months ending Feb. 29, 1912	
	lbs.	$	lbs.	$
Fertilizers (manufactured) . . .		134,063		413,905
“ (unmanufactured) .		19,155		3,151
Muriate and Sulphate of Potash	1,836,315	33,740	6,840,138	125,849
Kainit and other crude Potash Salts	726,917	5,868	985,750	9,252
Acid Phosphate	285,707	15,248	1,348,422	61,554
Phosphate Rock		8,000		43,774
Blast Furnace Slag		6,808		119,141
Sulphate of Ammonia	186,084	5,485	520,863	16,156
Nitrate of Soda	12,849,769	258,578	58,711,867	873,766
Nitrate of Potash	1,978,972	86,308	2,273,437	107,313

In the case of ‘‘manufactured’’ fertilizers and a few other items it has been impossible to get the quantities, the value only being given. ‘‘Unmanufactured’’ fertilizers represent those materials which could not be properly identified, and the decrease in the amount of these would indicate better classification facilities in recent years.

Acid Phosphate (non-medicinal) would seem to include a large proportion, not used for fertilizer purposes, since the value given is much in excess of the price of this material as a fertilizer.

Nitrate of soda is at present the most popular form of nitrogenous fertilizer, but the bulk of this material imported is used for manufacturing purposes, and it is yet impossible to even approximately estimate the amount used for fertilizer purposes.

Nitrate of potash is also almost entirely used for industrial purposes, its use as a fertilizer being very limited.

Unfortunately, no figures are available to show the production of fertilizers in Canada itself, but most of the slaughter house tankage and bone, formerly exported, is now, by the addition of potash, being converted into mixed-fertilizer for home consumption.

The importation of other fertilizer materials gives, however, a sufficient indication of Canada's increasing fertilizer consumption.

Pulp and Paper

In response to the growing demand for paper and pulp, Canada's output of these materials is growing rapidly. Stretching unbroken from the Atlantic to the Pacific are immense forests of spruce and balsam, the woods which are to-day most commonly used in this branch of manufacturing. When it is noted that numerous rivers and lakes throughout this territory offer at the same time, the means of transport and the supply of power, the present and future importance of Canada in the production of pulp and paper can be appreciated. The pulp mills are usually situated on rivers near the edge of civilization while the paper mills are as a rule near the industrial centres. The products are exported largely to the United States which is the best customer, and also to the United Kingdom. It is impossible to deal with so large an industry in detail, and some statistics are appended which will give an idea of the trade. No figures regarding paper are available.

1910	Quebec	Ontario	Nova Scotia	New Brunswick	British Columbia	Total
Pulp production	282,938	156,076	25,955	9,285	350	474,604
Mechanical pulp	235,889	108,351	25,955			370,195
Sulphite pulp	40,681	47,271		7685	350	95,987
Soda Pulp	6368	454		1600		8422
Spruce used, cords	239,824	189,196	25,636	15,134	440	470,230
Balsam " "	96,474	20,256	3745			120,475
Plants	25	15	6	4	1	51

Wood pulp exported—328,977 tons, value $5,694,896.

1911.

Mechanical pulp produced, tons	362,321
Sulphite " " "	110,391
Soda " " "	24,121

THE RUBBER INDUSTRY

The manufacture of rubber goods is carried on by three companies:

The Gutta Percha & Rubber Mfg. Co. of Toronto,
The Dunlop Tire & Rubber Co. of Toronto,
The Canadian Consolidated Rubber Co. of Montreal.

The last named Company is a merger of a large number of smaller companies with plants at Bowmanville, Port Dalhousie, and Berlin in Ontario, and Granby, Quebec. The capital invested is about $8,800,000, and the number of employees is approximately 4,000. The output for 1911 was over $18,500,000.

The products manufactured include a large range of rubber goods, such as rubber footwear, mechanical rubber goods of almost every description, automobile tires, and so forth.

A recent development which may be mentioned under this heading is the manufacture of Bakelite by Plastics, Limited, of Toronto. As is well known, this is a condensation product of phenol and formaldehyde, the preparation of which is the invention of Dr. L. H. Baekeland. His patents in America are controlled by the American Bakelite Company, of New York, which has sold its rights in Canada to the above Company. The plant has not been in operation very long, but it is already manufacturing a large number of products which have hitherto been made of ebonite or fiber, such as parts for motors, switches, and high tension apparatus in general, as well as insulating varnishes, etc.

COMPRESSED AND LIQUEFIED GASES

The most important product of this class is liquid carbon dioxide. The Canadian Carbonate Company, of Montreal, and the Dominion Carbonic Company, of Toronto, are the only firms engaged in the manufacture of this gas. The former utilizes the calcination of magnesite rock, and the latter, the combustion of coke. In each case, the gas is purified and compressed into steel cylinders for shipment to bottlers, brewers, and soda fountains. The combined output of the two plants for 1912 has been estimated at 2,500,000 pounds of liquid gas, with a gross value of about $150,000.

Liquefied ammonia is produced on a commercial scale by the Dominion Tar and Ammonia Co., Hamilton, but there has been a notable extension in recent years of the compressor system of artificial refrigeration and a large amount of the liquefied gas is being utilized in the manufacture of ice and in many cold storage plants. No data are, however, available as to the actual extent of the industry.

STARCH

The manufacture of starch and starch products is carried on by two companies:

The St. Lawrence Starch Co., of Port Credit,
The Canada Starch Works, of Montreal.

The latter has one factory at Cardinal (known as the Edwardsburg plant) and another at Brantford. The Cardinal plant is said to be the largest in the British Empire, its output corresponding to about 2500 bushels of corn, or 75,000 pounds of starch, per day.

The combined output of both companies is about 1,000,000 pounds of starch, glucose and syrup per day. About 60 percent. of this output is syrup, the remainder consisting of starch and starch products. The process of manufacture presents no special features; a description of the practice at these plants will be found in a paper by Dr. Kaufmann which was presented about two years ago before the Society of Chemical Industry. The by-products obtained are cattle foods and oil which is used in the manufacture of linoleums, etc.

Extraction and Refining of Metals

The metallurgical industry of Canada is as yet only in its beginning, although it has grown very rapidly during the past twenty-five years. In 1886, the total metallurgical production of Canada was valued at approximately $8,000,000; in 1893 it had grown to double this amount, and in 1910 it amounted to nearly $50,000,000. The production of the more important metals during 1910 and 1911 is shown in the following tabulated statement:[1]

	1910		1911	
	Quantity.	Value.	Quantity.	Value.
		$		$
Copper . . . . Lbs.	55,692,369	7,094,094	55,848,665	6,911,831
Gold . . . . Ozs.	493,707	10,205,835	. . . .	9,762,096
Pig iron . . . . Tons.	800,797	11,245,622	917,535	12,306,860
Lead . . . . Lbs.	32,987,508	1,216,249	23,525,050	818,672
Nickel . . . . “	37,271,033	11,181,310	34,098,744	10,229,623
Silver . . . . Ozs.	32,869,264	17,580,455	32,740,748	17,452,128
Other metallic prodcuts	. . . .	510,081	. . . .	409,674
Total	. . . .	59,033,646	. . . .	57,890,884
Less pig iron credited to imported ores	695,891	9,594,773	875,349	11,693,456
Total metallic	. . . .	49,438,873	. . . .	46,197,428

The subdivision of the mineral production in 1910 and 1911, by provinces, was approximately as follows:[2]

---

[1] Bulletin No. 150, Department of Mines; Preliminary Report on the Mineral Production of Canada during 1911.

[2] Ibid, p. 6.

Province	1910		1911	
	Value of Production.	Per cent of Total.	Value of Production.	Per cent of Total.
	$	%	$	%
Nova Scotia	14,195,730	13.29	15,354,928	15.01
New Brunswick	581,942	0.54	611,597	0.60
Quebec	8,270,136	7.74	9,087,698	8.88
Ontario	43,538,078	40.76	42,672,904	41.72
Manitoba	1,500,359	1.40	1,684,677	1.65
Saskatchewan	498,122	0.47	618,379	0.60
Alberta	8,996,210	8.42	6,404,110	6.26
British Columbia	24,478,572	22.92	21,237,801	20.76
North West Territories	4,764,474	4.46	4,619,592	4.52
Dominion	106,823,623	100.00	102,291,686	100.00

Gold. The history of gold mining in Canada has been somewhat similar to that in California and Australia. Simultaneously with the exploitation of the gold fields of California, placer mining received a great impetus in British Columbia, and at one time a considerable amount of gold was derived from this region. Later on, about 1896, the Klondike was found to contain gold and the gold production rose rapidly, attaining a maximum value in 1900. As the placer deposits of this district became exhausted, the total production of the Dominion fell off from over $27,000,000, in 1900, to $8,000,000, in 1909. Within the past two years, however, the gold production of the Yukon has been increasing, and it is reasonable to suppose that it will continue to increase, owing to the extensive scale on which dredging and hydraulic mining are being carried on.[1]

While the Yukon territory yields about half the total gold production of Canada, British Columbia supplies almost the whole of the remainder. Most of the gold produced in the latter province is derived from auriferous copper pyrites ores in the Nelson and Rossland districts, only about ten per cent. being obtained from placer deposits.

---

[1] Commission on Conservation, Canada. Report on Lands, Fisheries and Games, p. 407.

Both Ontario and Nova Scotia were at one time important producers of gold. In the former province the production rose as high as $421,591 in 1899, and then fell steadily to $188,036 in 1903. Since that year the production has rarely exceeded $66,000, and in 1911 it amounted to approximately $38,000. The production of Nova Scotia has decreased from over $600,000, in 1899 to $142,000 in 1910.[1]

The following table gives the production for 1909, 1910 and 1911, by provinces:

Province.	1909.	1910	1911. (estimated)
Nova Scotia	$210,711	$163,891	$142,000
Quebec	3,990	2,565	12,443
Ontario (b)	32,425	63,849	37,929
Alberta (a)	525	1,850	
British Columbia (c)	1,174,579	5,403,318	4,989,524
Yukon (a)	3,960,000	4,570,362	4,580,000
Total	9,382,020	10,205,835	9,761,896

(a) Placer gold.
(b) Gold from vein mining.
(c) Gold from placer and vein mining.

That the gold resources of the Yukon and British Columbia have only been skimmed, as it were, is evident from the fact that the mountain ranges of this territory in which gold deposits have been found so far form the northern extremity of the "western or Cordilleran belt which, extending from South America to Alaska, is recognized as one of the greatest mining regions in the world—noted principally for its wealth in gold, silver, copper, and lead." In both Mexico and the United States this mountain range has yielded about $3,000,000 per mile of its length, and it is only reasonable to expect that Canada, which possesses over 1,300 miles of this range, will yield enormous amounts of the precious metals in the future. The resources of placer gold in the Klondike alone have been estimated at $100,000,000. Up to the present probably not one-twentieth of this vast area has been prospected in detail.[1]

---

[1] Bulletin No. 88, Department of Mines; Annual Report on the Mineral Production of Canada for 1909, pp. 44–48.

Silver and Cobalt

The total silver production of the Dominion for 1911 is estimated at 32,740,748 ounces, valued at $17,452,128 of which 30,761,690 ounces were from Ontario, 1,910,323 ounces from British Columbia, 50,300 ounces from the Yukon and 18,435 ounces from Quebec.

Since the discovery of the deposits at Cobalt, Ontario, in 1904, the production of the country has grown rapidly, and Canada now ranks third among the silver-producing countries of the world. Ores from the Cobalt district are at present being treated at three metallurgical works, operated by the following companies:

The Canadian Copper Co., at Copper Cliff, Ont.,
The Deloro Mining and Reduction Co., at Deloro, Ont.,
The Coniagas Reduction Co., at Thorold, Ont.

"These three smelting works receive most of the high grade ores produced by the mines, as well as a considerable proportion of the concentrates, the shipments of low grade ores continuing for the most part to go to smelters in the United States, where their siliceous contents render them desirable for mixing with more basic material."[2]

Silver bullion of fineness varying from 850 to 998.2 is produced at the works, other products being white arsenic, and in the case of the Coniagas plant, nickel and cobalt oxides. During 1910 these three companies combined treated 9,466 tons of ore and concentrates, the silver recovered amounting to 14,574,837 fine ounces. "The remainder of the output, consisting of 24,893 tons of ore and concentrates, yielding 16,076,580 ounces of silver, was exported mainly to the United States. The material sent abroad for treatment thus contained on an average 645 ounces per ton, while that refined at home carried an average of 1,539 ounces per ton."[1]

---

[1] S. Dushman, Trans. Am. Electrochem. Soc. 20, p. 430.

[2] Report of Bureau of Mines, Ontario, 1910, p. 15.

The ores of the cobalt district are extremely complex and the problem of treating them so as to economically extract the silver, cobalt, nickel, and arsenic, is still awaiting a solution. At the present time the elements other than silver in these ores are of comparatively slight value, at any rate to the miners of the ore.[2] The demand for cobalt and arsenic is not great enough to keep pace with the amount produced as by-product during the extraction of the silver. "In fact, one year's operation of the cobalt mines will produce ore enough to meet the present consumption of cobaltic oxide for several years.[3] Some idea of the extent of this over-production of both cobalt and arsenic may be gathered from the fact that the ore contains on the average 6.76 percent. cobalt, 3.72 percent. nickel, and 30 percent. arsenic.[4]

Both the Canadian Government and the miners have consequently attempted to devise and encourage methods for utilizing these constituents. As a result of the bounty on cobalt oxide of 6 cents per pound of metallic cobalt content, both the Deloro Mining and Reduction Co. and the Coniagas Reduction Co. made shipments of the oxide in 1910.[5] The cobalt oxide, mixed with nickel oxide, is exported to Europe for use in the manufacture of china ware. The quantity of oxide, however, consumed in this manner is believed not to exceed 300 or 350 tons per annum, which is much below the equivalent of ore produced by the silver mines of Cobalt.

Attempts have been made to find an application of cobalt as a constituent of alloys, and a recent report would seem to point to the alloy with chromium as possessing a number of useful properties. According to this report, an alloy containing 25 percent. chromium and 75 percent. cobalt is superior to steel for knife blades and is very resistant to corrosion. "It is equalled in this respect only by gold and the metals of the platinum group." Mr. Haynes, the inventor of the alloy, regards it as particularly suitable for the manufacture of small cutting instruments, since it takes an edge comparable to that of tempered steel. He also suggests its use in the chemical and physical laboratory in place of platinum. It may therefore be that in this or similar directions an outlet will be found for the cobalt which the mines of the district of that name are now forcing upon an unwilling market.[1]

---

[1] Ib, 1911, p. 13.
[2] Ib, 1909, p. 13.
[3] Ib, 1910, p. 24.
[4] Ib, 1911, p. 17.
[5] Ib, 1911, p. 25.

Arsenic

At one time all the arsenic manufactured in Canada was obtained from auriferous arsenic pyrites in Hastings County, Ontario.[2] But in recent years the reduction works at Copper Cliff, Deloro and Thorold have supplied the total demand for this product. During 1910 these plants recovered and marketed 1,524 tons of white arsenic, valued at $70,709, an average of 2.31 cents per pound.[3] As in the case of cobalt, the consumption of arsenic has not kept pace with the enforced increase in supply, and since the opening of the cobalt mines the price has fallen from six or seven cents per pound to less than three cents.

Copper and Nickel

Copper in the refined state is not produced in Canada. The ores are smelted to a matte containing gold and silver as the valuable constituents, which is then exported to the United States for refining. The production of the Dominion is derived from the provinces of British Columbia and Ontario.

In the former province, "gold-copper" ores occur in the Rossland and Boundary districts. "The average content of these ores is rather less than 30 pounds per ton; but with present treatment facilities, it is possible to smelt 9,000 tons of ore daily, while with the smelter improvements and additions now being made, or contemplated, this output will probably be increased within the next two years to 10,500 tons, or a possible production of 100,000,000 pounds of copper per annum."[1] At the present time the following smelting companies are established:

---

[1] Ib, 1911, p. 25.

[2] W. R. Lang, The Chemical Industries of the Dominion, Trans. Can. Institute, *8*, 151–190 (1905); Journ. Soc. Chem. Ind. 1904.

[3] Report of Bureau of Mines, Ontario, 1911, p. 33.

The Brittania Copper Syndicate, Limited.
Head Office—Brittania Beach, B. C.,
Smelter—Crofton, Vancouver Island;

The British Columbia Copper Company, Limited.
Head Office—New York,
Smelter—Greenwood.

"The works comprise a thoroughly modern well-equipped plant of three furnaces, having a capacity of 2000 tons of ore daily, and two converters, equal to a capacity of about 2500 pounds of copper per hour, working on matte of 45 percent. copper content."[2] The product from the converter is blister copper and is sent to the Nicholls Chemical Company, New York, to be refined.[3]

The Consolidated Mining and Smelting Company, of Canada, Limited.
Head Office—Toronto, Ont.
Smelter—Trail, B. C.

"The present works is a completely equipped and modern plant, designed to treat all grades of copper and lead ores, and includes a refinery for producing pig lead, as well as refined silver, gold, and antimony, with copper sulphate as a by-product."[4]

Dominion Copper Company.
Head Office—New York.
Smelter—Boundary Falls, near Greenwood, B. C.

---

[1] Bulletin No. 24, Department of Mines; Report on the Mining and Metallurgical Industries of Canada, 1907–8, p. 137.

[2] Ib., p. 232.

[3] W. R. Lang, loc. cit., p. 157.

[4] Bulletin No. 24, Department of Mines, p. 235.

The Granby Consolidated Mining, Smelting, and Power Company, Limited.
Head Office—Grand Forks, B. C.
Smelter— " " "

This is the largest of the smelting works in British Columbia. It employs about 300 men at the smelter, besides 500 men at the mine. The plant is capable of treating 4000 tons of copper ore daily. Both matte and blister copper are produced. The former averages between 40 and 44 percent. copper; 10 to 15 ounces of silver, 1.6 and 2.6 ounces of gold per ton, while the latter carries 99.5 to 99.6 percent. copper, 25 to 37 ounces of silver, and 4 to 6.5 ounces of gold per ton.[1]

During 1910 this company produced 11,407,351 pounds of blister copper, containing 30,945 ounces of gold and 227,445 ounces of silver.[2]

The total capitalization of the above smelters is about $30,000,000 and the aggregate number of men employed by them is about 1100. The production of blister and matte copper from the province during 1911 was approximately 35,500,000 pounds.[3]

The copper production of Ontario is mainly derived from the nickel-copper ores of Sudbury. "At present there are only two companies, the Canadian Copper Company, and the Mond Nickel Company, engaged in active smelting operations. Both these companies produce a nickel-copper matte from a nickeliferous pyrrhotite ore, which carries in addition values in copper. The matte is shipped to refining works in the United States and England for subsequent treatment."[4]

The Canadian Copper Company is an American corporation, with head office at Cleveland, Ohio. The smelting works are located at Copper Cliff, near Sudbury, and constitute "one of the largest and best-equipped plants of the kind to be found anywhere, costing in the neighborhood of $4,000,000. Power for operating the mines and works is developed at High Falls on the

---

[1] Ib, p. 252.

[2] Private communication.

[3] Bulletin No. 150, Department of Mines, p. 11.

[4] Bulletin No. 24, Department of Mines, p. 383.

Spanish river, about 28 miles from Copper Cliff, where there is a natural drop of about 65 feet, increased by damming to 85 feet. About 12,000 horse power can be obtained here, and costs delivered at Copper Cliff about $15. per horse power-year. Ore is taken for the most part from the Creighton mine, which furnished 391,575 tons out of the 508,404 tons raised by the Company in 1910. This ore contains about 1.5 percent. copper, and 4.5 percent. nickel."[1] After many years of experience, a very efficient method of treating these complex nickel ores has been developed and a matte is produced containing about 35 percent. copper-nickel, 27 percent. sulphur, and the balance iron. Through subsequent bessemerizing this matte is reduced to about 40 to 49 percent. nickel, 26 to 49 percent. copper, 12 to 23 percent. sulphur, and 0.5 to 2 percent. iron. The smelter treats about 1000 tons of ore per day. All the copper-nickel matte produced is sent to the refinery of the Orford Copper Company, of New Jersey, U. S. A.[2]

The Mond Nickel Company's smelting plant is at Victoria Mines on the Sault branch of the Canadian Pacific Railway. The Company owns altogether 7000 acres of mining lands, partly leased and partly in fee simple. The average analysis of the run of mine ore is about 2½ percent. nickel, and 2½ percent. copper. The capacity of the smelter was about 310 tons of high grade matte per month in 1908.[3] "The bessemer matte produced contains about 40 percent. copper and 40 percent. nickel, about 15 percent. iron, and the balance sulphur and impurities. This matte is put up in barrels and shipped to Swansea, England, to the Mond Refining Works."[4]

The discovery of the copper-nickel ores in the Sudbury district has placed Ontario in the position of being the largest producer of nickel in the world, these deposits now supplying about 75 percent. of the world's total. The production of nickel-copper matte for 1909 and 1910 is contained in the following table:[5]

[1] Report of Bureau of Mines, Ontario, 1911, p. 26.

[2] Bulletin No. 24, Department of Mines, p. 389.

[3] Ib., p. 398.

[4] W. R. Lang, loc. cit., p. 158. Also contains description of Mond's process for extracting nickel from its ores.

[5] Report of Bureau of Mines, Ontario, 1911, p. 27.

		1909	1910
Ore raised	Tons	451,892	652,392
" smelted	"	462,336	628,947
Bessemer matte produced	"	25,845	35,033
Nickel contents	"	13,141	18,636
Copper "	"	7,873	9,630
Value of nickel		$2,790,798	$4,005,961
" copper		1,122,219	1,374,103
Wages paid		1,234,904	1,698,184
Men employed		1,796	2,156

The statistics for 1911 are not yet completed, but it is estimated that the production is about the same as for 1910.

An interesting development in connection with this industry is the production of "Monel Metal," an alloy of nickel and copper which has been placed on the market by the Canadian Copper Company, and which is produced by that Company directly from the matte. "In fact, it is asserted that the proportions in which the nickel and copper occur in the Canadian Copper Company's ores are almost precisely those required for the alloy, which are about 67 percent. nickel, and 37 percent. copper, and that by careful attention to the furnace charge a Bessemer matte can be produced within one percent. of that required in making Monel metal. Considerable quantities of this alloy are now coming into use. It is claimed to possess great strength and to be practically non-corrodible."[1]

Iron

"The Canadian iron industry dates back to the establishment of the St. Maurice forges by the French Government in 1737. Many other minor plants were subsequently built, but they all failed in consequence of the competition of Great Britain and the United States. This early failure was due as much as anything else to lack of enterprise, capital, and proper shipping facilities. The modern development of the industry may be said to date from the introduction of a protective duty on iron in 1887. The granting of bounties by the Dominion and Ontario governments has also assisted largely in bringing about the present condition of the iron and steel industries."[1]

---

[1] Ib, p. 28.

The production of pig iron by provinces in 1910 and 1911 was as follows:

PRODUCTION OF PIG IRON BY PROVINCES, 1910 AND 1911

Provinces	1910			1911		
	Tons	Value $	Value per Ton $	Tons	Value $	Value per Ton $
Nova Scotia..	350,287	4,203,444	12.00	390,242	4,682,901	12.00
Quebec......	3,237	85,255	26.34	658	17,282	26.34
Ontario......	447,273	6,956,923	15.55	526,635	7,606,674	14.44
Total....	800,797	11,245,622	14.04	917,535	12,306,860	13.41

The following table shows the origin of the raw materials utilized in producing this iron in 1911.[2]

Material	Domestic	Imported
Ore..................................	67,434	1,628,368
Coke................................	543,933	577,388
Limestone...........................	625,216	

It is thus seen that this industry is to a large extent dependent upon imported raw materials. Nearly all the ore used in Nova Scotia is imported from Newfoundland, while a great deal of that used in Ontario is derived from the south shore of Lake Superior.

---

[1] W. R. Lang, loc. cit., p. 153.

Dominion bounty on pig iron, $3 per ton produced. Ontario bounty $1 per ton on pig iron produced from Ontario ores, and 50 cents on ores not obtained in the Province; the rate of $1 to be only paid up to 25,000 tons.

[2] Bulletin No. 150, Department of Mines, p. 15.

The classification of the production according to the purpose for which it was intended was as follows:

Bessemer 208,626 tons; basic 464,220 tons; foundry and miscellaneous 244,686 tons.

The history of the iron and steel industry in Ontario forms an attractive chapter in the evolution of Canadian industry. The story down to 1904 has been told interestingly by Prof. W. R. Lang.[1] A detailed account of the industry, not only from an historical but from an economical, geological and metallurgical point of view, is to be found in the Report of the Bureau of Mines of Ontario, 1908, pp. 190–342, from which source a great deal of the information has been derived regarding the individual plants.

At the present time there are eight furnaces producing pig iron in Ontario, distributed as follows: Algoma Steel Company, Sault Ste. Marie, two; Hamilton Steel and Iron Company, Hamilton, two; Atikokan Iron Company, Port Arthur, one; Canada Iron Corporation, Midland, two; Standard Chemical Company, Deseronto, one. The combined production of these plants in 1911 was 526,610 tons of pig iron. Of the ore smelted, 67,631 tons were of domestic and 848,814 of foreign origin.[2]

The Hamilton Steel and Iron Company and the Algoma Steel Company were also producers of steel. The steel produced in 1910 (the last year for which data are available) amounted to 331,321 tons, valued at $7,855,407. The total number of workmen employed in the iron and steel industry in Ontario was 2,120 in 1910, over $1,400,000 being paid in wages.[3]

The plant of the Algoma Steel Company, which is owned and operated by the Lake Superior Power Corporation, is situated at Sault Ste. Marie on the St. Mary's River, and consists of two blast furnaces, of 250 tons capacity per day, with all necessary modern stock handling machinery, two acid bessemer converters, two basic open hearth furnaces and a rail mill with an annual capacity of 225,000 tons. The ores used are obtained almost entirely from the Lake Superior American ranges, and the coke used is derived from the West Virginia fields. The limestone is quarried in Michigan about 40 miles from the Sault. The company also has under construction a 400 ton furnace, a 12″ and 18″ merchant mill, and a complete installation of by-product coking ovens (110 ovens, Koppers type, with capacity of 1,100 tons of coke per day).

---

[1] W. R. Lang, loc. cit., pp. 153–4.

[2] Bureau of Mines, Ontario; Preliminary Report on the Mineral Production of Ontario for 1911.

[3] Report of Bureau of Mines, Ontario, 1911, p. 29.

"The works of the Hamilton Steel and Iron Company, Limited, are located in Hamilton, on the shores of Burlington Bay, Lake Ontario, and in point of size and investment come next to those of the Algoma Steel Company. The plant consists at present of two coke blast furnaces, four basic open hearth furnaces, puddling furnaces, rolling mills and a forging department, also a small spike mill. . . . Latterly, all ores have been secured from the Lake Superior American ranges and from the Helen mine in Michipicoten, Ontario. Coke is obtained from the Pennsylvania Connellsville district. Limestone is obtained from several localities not far from Hamilton. Dolomite from the Dundas quarries is used for the blast furnaces, and from the St. Mary's quarries in Perth and Port Colborne quarries in Welland are obtained the limestones for open hearth work." The two blast furnaces have a combined capacity of over 525 tons per day. Two of the open hearth furnaces are of 40 tons and two of 20 tons capacity, all are of the stationary type and are fired with natural gas. The whole plant produces annually over 180,000 gross tons of pig iron, 100,000 net tons of steel ingots, and 100,000 gross tons of rolled iron and steel, besides forgings, railing car axles, and track spikes.

The Canada Iron Corporation has a plant situated on the shore of Midland Harbor. About 50 to 75 percent. of the ore used is imported from the Lake Superior district; coke is brought in from the Connellsville district in Pennsylvania, while the limestone is quarried about five miles from the furnace on the eastern shore of Midland Bay. The capacity of the two furnaces in operation is 375 tons.

The blast furnace at Deseronto was formerly blown with charcoal as fuel, this being supplied by the Standard Chemical Company, Limited, which manufactures charcoal and its by-products. In 1907, owing to failure of the wood supply, it was decided to manufacture coke iron and at the present time part of the fuel is imported from Connellsville. The ores are obtained mainly from the American Lake Superior ranges, arriving via the Welland Canal. Limestone is obtained from quarries along the Bay of Quinté railway, Ontario. The output of the furnace is about 35 gross tons of iron per day.

"Of late years considerable attention has been given to the deposits of iron ores that are found in the Thunder Bay and Rainy River districts of northwestern Ontario. Various projects were put forward for the utilization of these ores, but it remained for the Atikokan Iron Company, organized in 1905, to demonstrate the practicability of roasting and smelting the high sulfur magnetites of the Atikokan range for the production of foundry iron."[1] The plant located in Port Arthur comprises a blast furnace of maximum capacity of 200 tons per 24 hours, an ore roaster operated by the blast furnace gas, and a battery of 100 beehive coke ovens. The coal for the coke is obtained from the West Virginia fields, and the limestone is obtained from Kelly Island in Lake Erie.

This completes the survey of the plants at work in Ontario. Turning to the province of Nova Scotia, we find that there are three plants in operation.

The Dominion Iron and Steel Company was organized in 1899, with the intention of providing a larger market for the output of the Dominion Coal Company. The works are situated at Sydney, N. S., and include five blast furnaces of 280 tons capacity each, ten 50 ton open hearth furnaces of the H. H. Campbell tilting type, a 26" blooming mill and pit furnaces, a 28" rail mill, 1000 tons capacity, a rod mill of over 7000 tons capacity monthly, a continuous billet mill, of 600 tons daily capacity, 500 coke ovens, coal-washing, sulphuric acid plants, and by-product plant. The erection of a sixth furnace has been arranged for, the completion of which will give this company a capacity of over 400,000 tons per annum.

The principal source of the iron ore supply is Wabana mine, Bell Island, Newfoundland, some 400 miles from Sydney. This mine is estimated to contain 28 million tons of available ore, besides areas under the sea which are believed to be very extensive. It is estimated that the cost of this ore in stock bins at Sydney, C. B., is $0.817 per ton.[1] "Analyses of the ore show it to contain fifty percent. of iron, little sulphur, but rather too much silica, aluminum, and phosphorus. The result is a pig iron too high in phosphorus, but during the subsequent conversion of the pig iron into steel in open-hearth furnaces, this impurity is eliminated, and a fine quality of steel produced. For the best kind of pig iron, it is necessary to mix other ores with it, and for this purpose Cuban, Spanish, and Swedish ores are used, the result being a low phosphorus pig."[2]

---

[1] Ib, 1908, p. 319.

Limestone is obtained from the Company's quarries at Bras d'Or Lakes, about 85 miles by water from the works. It analyses about 94.6 percent. $CaCO_3$, with about 3 percent. $MgCO_3$. The supply of dolomite is derived from the Company's quarry at Scotch Lake, about 16 miles from Sydney.

Coal is obtained from the Dominion Coal Company's fields near at hand, at a cost of $1.24 per ton. The coke oven plant consists of ten batteries of fifty ovens each, of the Otto-Hoffman by-product type. The total capacity is rated at 1,200 tons of 37 hour coke per day of 24 hours. These ovens are of the latest type and are provided with a condensing house, a cistern, and the necessary coolers, scrubber, sieve washer, etc., for cooling and cleansing the gas and extracting from it the tar and ammonia. The latter is converted into sulphate of ammonium by neutralizing it with sulphuric acid. The greater part of this product is exported to the West Indies, where it is used as a fertilizer on the sugar plantations. The acid plant, which has a capacity of 40 tons per day, is a modification of the old chamber system, pyrites and sulphur being used as raw materials. The tar is pumped to storage tanks, and sold to the Dominion Tar and Chemical Company, Ltd., who have their works on the Dominion Steel Company's property, and near the coke ovens.

The number of men employed on the works of the Dominion

---

[1] Bulletin No. 24, Department of Mines, p. 537.

[2] W. R. Lang, loc. cit., p. 155.

Iron and Steel Company at Sydney, and at Bras d'Or Lakes, is over 4,000.

The Londonderry Iron and Mining Company, Limited, situated in Colchester County, N. S., has the oldest plant in Nova Scotia, having begun operations in 1850. Only one furnace of 100 tons capacity is in operation. The ore is obtained from the Company's mines near at hand and consists of hematite, siderite, specular ore and ochrey ore. The coke is obtained from 97 coking ovens, having a total capacity of 150 tons per day.

The Nova Scotia Steel and Coal Company, Limited, operates one blast furnace having a capacity of 200 tons per day, at Ferrona, near New Glasgow, N. S., and three 40 ton open hearth steel furnaces and one 50 ton open hearth rolling furnace at New Glasgow. The latter are all of the Wellman-Seaver-Morgan Company type, arranged in one row, and the Siemens-Martin process is used. The product of the furnace, which averages 240 tons per day, is tapped into 50 ton ladles, from which it is poured into molds in a pit. Electric power is utilized by the works and is generated from steam.

The iron ore is mainly derived from the Wabana mine, on Bell Island, Newfoundland. It is a red hematite containing about 55 percent. metallic iron, 3.7 percent. alumina, about 1 percent. phosphorus, and only the slightest trace of sulphur. Limestone is obtained from the Company's quarry at Point Edward, Cape Breton. The Company also owns its own coal colleries in Pictou County. About 1800 men are employed at the Works and 2400 more at the mines and quarries.[1]

According to the report of the Department of Mines of Canada, there were 12 furnaces in blast December 31, 1911, out of a total number of 18. The aggregate capacity of the furnaces actually constructed throughout the Dominion is about 3600 tons per day.

Lead

The production of lead in Canada is almost entirely from British Columbia mines. Lead smelting in this province dates practically from 1894, when a smelter was erected at Pilot Bay, on Kootenay Lake, by the Kootenay Mining and Smelting

[1] Bulletin No. 24, Department of Mines.

Company. Two years later the Hall Mines, Limited, commenced operations at Nelson, B. C., and then followed in rapid succession the installation of smelters at Grand Forks, Greenwood, and Trail. In most of these plants the Huntington-Heberlein process for treatment of lead ores has been adopted, with more or less modification.

The Consolidated Mining and Smelting Company also operate an electrolytic lead refinery at Trail, using Betts' process. As a full description of the plant and process is readily available in numerous publications, it is unnecessary to go into details in this connection. Since 1902, when the plant was first installed, its capacity has grown from 50 tons to 100 tons per day, and it is now treating practically all the British Columbia lead ores. Pig lead, fine gold, fine silver, refined antimony, copper sulphate, and babbitt metal are produced at the refinery, and lead pipe also is manufactured there. The refined lead finds a market in Canada, the United States and the Orient. The Carter White Lead Company, of Canada, with works at Montreal, uses Trail lead exclusively.[1] The total value of the refinery output for 1910 and 1911, as well as detailed statistics of the individual products, is given in the following table:[2]

	1910	1911
Total Refinery Output	$2,160,911	1,731,874
Gold, ounces	13,298	15,260
Silver, "	1,798,960	1,325,294
Lead, tons	16,493	11,763

STRUCTURAL MATERIALS

With the enormous increase in population there has naturally occurred a rapid growth in the production of structural materials.

The most important of the materials which come under this heading is Portland Cement. The value of the production has grown from $18,000 in 1890 to over $7,500,000 in 1911, during which year 5,677,539 barrels (of 350 pounds net) were produced at an average price of $1.34 at the works.[1] This was an increase of 29 percent. over the production in 1910. Furthermore, the amount imported has decreased from 64 percent. of the total consumption in 1901 to only 7 percent. in 1910.

---

[1] Bulletin No. 88, Department of Mines, p. 88.

[2] Private communication.

According to returns to the Department of Mines in 1911 there were 22 plants operating in 1910, with a total daily capacity of 25,835 barrels.[2] These plants are distributed as follows: one in Nova Scotia, using blast furnace slag; one in Manitoba, making a natural Portland Cement; one in British Columbia, two in Alberta and three in Quebec, using limestone and clay; and fourteen in Ontario of which eleven use marl and three limestone.

The use of shell marl as the source of lime was the prevailing tendency at the outset of the industry. But more recently the tendency is strongly towards the use of solid rock, as "it has been found more economical to raise and grind the rock than to dredge the marl and handle the large proportion of water accompanying it."[3] This is well shown by the following statistics:

Year.	Cement from marl	Cement from limestone
1908	1,573,090	1,922,871
1909	810,706	3,336,002
1910	1,214,479	3,181,803

The method of manufacture is in most cases the standard American practice, involving the use of rotary kilns in preference to those of the stationary type.

The number of men employed in the cement industry is over 2200, and the wages paid about $1,300,000 per annum.

About 80 firms are engaged in the manufacture of lime throughout the Dominion. The average number of men employed in 1910 was reported as 976, and wages paid $466,876.[1] The annual production for 1909, 1910, and 1911 has been about 5 to 6 million bushels at an average value of 19 to 20 cents per bushel. About 50 percent. of this production is derived from Ontario.

---

[1] Bulletin No. 150, Department of Mines, p. 20.

[2] Bulletin No. 114, Department of Mines; The Production of Cement, Lime, Clay Products, Stone and other Structural Materials in Canada, 1910.

[3] Report of Bureau of Mines, Ontario, 1911, p. 32.

The manufacture of sand-lime brick was first started about six years ago. Since that time the number of operating plants has increased rapidly. In 1910 there were at least 13 firms producing sand-lime brick, the total annual production amounting to approximately 45 million, at an average value of $8.34 per thousand. Both vertical and horizontal presses are in use.

As the cost of producing this class of brick is much below that of clay brick, their manufacture forms a very profitable undertaking. When made from fine white sand, the product has a neat and clean appearance equal to that of the best pressed clay brick, and may be made with a crushing strength which is well over 2500 pounds per square inch.

Gypsum is found in considerable quantities in the provinces of Nova Scotia and New Brunswick. The tonnage of gypsum mined or quarried in 1910 was 548,019 tons, and the quantity calcined 69,889 tons.[2] "At Windsor, N. S., there are immense deposits; the beds found in the vicinity of Hillsborough, N. B., are, however, very large and of great purity, and form the basis of the most extensive operations. In manufacturing plaster of Paris, the stone is first dried in the air and ground—not burned in lumps as is still done to a considerable extent in England and on the Continent; and the pulverized materials subjected to a process of calcination in kettles, of a capacity of sixty barrels of 300 pounds of the calcined plaster, furnished with lids and stirring arms which keep the material in constant motion. When the required temperature has been reached (285°F.), the plaster is removed and packed in paper-lined barrels for market. Analysis of the Hillsborough gypsum shows it to be 99.88 percent. $CaSO_4.\ 2\ H_2O$."[3]

There is also a plant at Paris, Ontario, manufacturing plaster of Paris and various alabaster products from gypsum mined at Caledonia, Ontario.

---

[1] Bulletin No. 114, Department of Mines, p. 40.

[2] Bulletin No. 117, Department of Mines; Summary of the Mineral Production of Canada, 1910, p. 17.

[3] W. R. Lang, loc. cit., p. 174.

PETROLEUM

Petroleum occurs in commercial quantities in the counties of Kent and Lambton, in the province of Ontario; but the supply has been decreasing during the last few years. While in 1907 there were produced nearly 800,000 barrels of crude petroleum, the production had diminished to about 300,000 barrels in 1910. This decrease is due largely to the gradual diminution in the yield of the wells of the Lambton County field. The wells at Petrolea and Oil Springs have been producing oil for over forty years, and the average production per well is now very small, being not over eight or nine gallons per day.[1]

In 1905 oil was first struck in the new Tilbury field in the county of Kent, and later on oil was also drilled for in the Romney field. During the next two years the wells of these fields produced an average of about 30,000 barrels per month, which was about half of the total production for Ontario.[2] Subsequently the production fell off very rapidly, and in 1910 it amounted to only 5000 barrels (of 35 gallons) per month.

Petroleum has also been found in Quebec, Nova Scotia, New Brunswick and Alberta. The hopes which were at one time entertained that the North West would provide a supply that would counteract the diminution of the Ontario supply have so far not materialized.[3]

Crude oil is refined in Ontario by three companies:

The Imperial Oil Company, Sarnia.
The Canadian Oil Companies, Limited, Petrolea.
The British American Oil Company, Toronto.

The plant of the Imperial Oil Company has a capacity of 900,000 barrels of crude oil per annum. The oil, as it is received from the producers, is stored at the works in large reservoirs, from which the supply for the crude oil stills is drawn. These stills contain approximately 640 barrels of oil each, and produce as distillates benzine, gasoline, and refined oil.[1] It is interesting to note that it was in this plant that Frasch first worked out the copper oxide process for refining crude oil containing sulphur. Before this process was devised the Petrolea oils could only be sold for fuel purposes.

---

[1] Report of Bureau of Mines, Ontario, 1909, p. 33.

[2] Ib., 1907, p. 92.

[3] W. R. Lang, loc. cit., p. 180–1. See also Bulletin No. 88. Department of Mines, for report on Alberta oil fields.

The tar which collects at the bottom of the stills is further treated for the manufacture of lubricants and paraffin wax.

The Canadian Oil Companies have erected a very modern plant at Petrolea and obtain a large number of products by the refining of the crude oil.

As the output of domestic crude oil is quite inadequate to meet the requirements of these refineries, the deficiency is made up by imports from the oil fields of the United States. Thus the quantity of Canadian oil distilled in the above refineries in 1910 was nearly 14 million gallons, while of imported crude oil over 17 million gallons were distilled. The following statistics give details of the operations carried on by oil refining works at Sarnia and Petrolea.[2]

PETROLEUM AND PETROLEUM PRODUCTS

1909–1910

	1909	1910
Crude produced.................Imp. gal.	14,723,105	11,004,357
" distilled.................. "	35,530,918	36,171,032
Value crude produced....................	$559,478	$368,153
" distilled products..................	$2,501,384	$2,511,368
Illuminating oil.................Imp. gal.	17,902,254	18,983,357
Lubricating " .... "	3,856,778	4,469,038
Benzine and naptha....................	3,930,691	4,297,615
Gas and fuel oils and tar................	4,687,588	5,876,498
Paraffin wax and candles ....lb.	7,092,278	5,179,391
Workmen employed ....No.	436	428
Wages paid............................	$261,014	$280,485

---

[1] Bulletin No. 24, Department of Mines, p. 439.

[2] Report of Bureau of Mines, Ontario, 1911, p. 38.

REFINED CHEMICALS AND DRUGS

At the present time there are three firms in Canada which devote part of their time to the manufacture of fine chemicals. In two of these cases this line of manufacturing is a side issue in the manufacturing of pharmacopoeie preparations and pharmaceutical products, while in the third case it is part of a general chemical business. The sale of fine chemicals so manufactured is estimated at $175,000 per year.

The following are the principal lines manufactured at the present time: Iodides and Iodine Preparations, Silver and Gold Salts, Salts of Mercury, Hydrogen Peroxide, Phosphates of Soda, Sulphites and Bisulphites, Amyl Acetate.

On account of the exigencies of the Canadian market, which demands a very wide range of material, a number of smaller lines are made which will not be enumerated here, their manufacture taking place from time to time, and not continuously, as a rule, on a steady scale.

The greater proportion of what may be classed as fine chemicals used in Canada at the present time is imported. The principal countries of origin are Great Britain, which enjoys preferential duty, Germany, United States, and France.

The Canadian market for products coming in, of this class, is, however, increasing rapidly, and it seems reasonable to suppose that the manufacture of the same will be undertaken with greater energy as the market develops.

The manufacture of pharmaceutical products in Canada is being carried on aggressively at the present time by a number of firms, some of whom, as their names will indicate, are branches of houses having headquarters in other countries. From the number of firms operating, it will be seen that this field is fairly well occupied at the present time. The steady growth of the different firms interested in this line of manufacture is an evidence of a growing market for the products which they make.

The following is a list of the principal firms operating in Canada:

Park Davis & Co., Limited, Walkerville, Ont.
Frederick Stearns & Co., Ltd., Windsor, Ont.
Lyman Bros. & Co., Ltd., Toronto

Toronto Pharmacal Co., Ltd., Toronto
Moyes Chemical Co., Ltd., Toronto
H. K. Wampole & Co., Limited, Perth, Ont.
National Drug & Chemical Co. of Canada, Ltd. Head Office, Montreal, with branches in the principal cities of Canada
Chas. H. Frosst & Co., Montreal
Shuttleworth Chemical Co., Toronto
Ingram & Bell, Toronto
United Drug Co., Toronto
Wyeth & Co., Montreal.

The enumeration of the lines manufactured is far too long for this publication. It is sufficient to say that the firms mentioned above confine their activities to three general classes of pharmaceutical products. In the first class we may include the standard preparations of the pharmacopoea. In the second class we may include standard preparation of a non-secret character. The third class consists of proprietary and other preparations made by the above named firms, but not always sold by them direct.

SULPHURIC, NITRIC AND HYDROCHLORIC ACIDS, ETC.

Canada manufactures practically all her acids, the amount imported being very small. While the demand for these and similar heavy chemical products has been moderate in the past, it is increasing very rapidly, and there is every reason to suppose that the future will see an enormous expansion in this line of manufacture. But even at the present time the manufacture of the heavy acids may be said to be the most important, as far as the chemical industry is concerned in this country.

The manufacture of these products is carried on both by companies of which the capital is purely Canadian and also by others which are branches of large foreign concerns. It is impossible, therefore, to state accurately the amount of capital which is employed in this business in Canada.

The following is a list of companies with their branches which are operating along these lines in this country:

The Nichols Chemical Company. Head Office for Canada, Montreal. Works situated at Sulphide, Ont., Capleton, Quebec, and Barnet, B. C. Products manufactured Sulphuric, Nitric and Hydrochloric Acids, Mixed Acids, Salt Coke and Glauber Salt.

Victoria Chemical Company, Victoria, B. C. The products manufactured include the above acids, Glauber Salt, and Lime Sulphur Spray.

Grasselli Chemical Co., Hamilton, Ont. This Company manufactures the heavy acids, arsenate of lead and lime sulphur spray.

Algoma Steel Co., Sault Ste. Marie, Ont. Manfacturers of sulphuric acid and ammonium sulphate.

Explosives

While this is not a large business in Canada, it is carried on mostly by three companies. There have been a number of factories built by other companies which were in the nature of experimental plants for the manufacture of explosives, but so far they have not been approved by the consuming public. No attempt has been made to enumerate the latter. The following firms are the principal manufacturers at the present time:

Canadian Explosives, Limited. Head Office, Montreal. Branches at Belle Isle Province, Quebec, Baudreul, P. Q., Vancouver, B. C.

Curtis Harvey, Limited, Rigaud, P. Q.

Dominion Explosives, Limited, Sand Point, Ont.

Electrolytic Alkali and Chlorine

"An electrolytic alkali industry was attempted about twelve yeas ago by the Lake Superior Power Co. Among the many subsidiary organizations initiated by this Company was the Canadian Electrochemical Company, for the electrolytic manufacture of caustic soda and bleaching powder. One hundred and twenty cells of the Rhodin mercury type were installed, each cell utilizing 1000 amperes at 5.5 volts. The total capacity of the plant was 4.5 tons of caustic and 9 tons of bleaching powder per day. The salt was obtained from wells in the county of

Huron. The work was discontinued at the time when it became necessary to reorganize the whole Lake Superior corporation, and has not been renewed since then. There was then, as now, no protection for caustic soda."[1]

At the present time the Canadian Salt Co., of Windsor, Ont., has an electrolytic alkali plant at Sandwich. The Gibbs cell is said to be used, but no further data are available.

ELECTRIC FURNACE PRODUCTS

The low cost at which hydro-electric power may be obtained in a large number of localities throughout the country has led to the establishment of a number of electrochemical industries, especially in Ontario and Quebec, where both raw materials and water power facilities are readily available.

Calcium Carbide

This constitutes the oldest electrochemical industry in Canada. Very recently the three plants operating at Thorold, Ont., at Ottawa, Ont., and at Shawinigan Falls, Que., have amalgamated as the Canada Carbide Company, Limited, with a capitalization of $2,000,000. The plant at Thorold has been in operation since 1897. Six furnaces are in operation, each requiring from 2500 to 3000 amperes at 75 volts. The voltage is regulated automatically by special devices. After fusion of the charge, which consists of lime, coke and coal, the furnace is dumped and the unfused material re-treated. The carbide is obtained in the form of a solid fused mass, which is crushed and bolted and finally packed into steel receptacles, each containing 100 pounds. Power is obtained from three power stations on the Welland Canal, near by. The total capacity of the plant is about 1200 tons of carbide per annum.

The plant at Ottawa is located on Victoria Island, the power being supplied by the Ottawa Power Company. The capacity of the plant is 3000 to 4000 tons per annum.

Shawinigan Falls, situated about 85 miles east of Montreal on the St. Maurice River, supplies about 25,000 H.P., most of which is transmitted to Montreal at 50,000 volts. Part of this power is, however, utilized locally by the carbide plant and that of the Northern Aluminium Company.

---

[1] S. Dushman, loc. cit., p. 423.

The former is situated at a distance of two miles from the power house of the Shawinigan Water and Power Company. "The electric furnaces operate continuously: the manufactured carbide is drawn off in pots, and the fused mass, after cooling, is broken up and granulated in mills. Eight furnaces have been installed, two of which require each 1,500 H.P. for their operation. The combined capacity of the furnaces is 25 tons of carbide per day, requiring a total of 7500 H.P."[1]

The three plants produced over 8000 tons of carbide during 1911, and it is estimated that the production for 1912 will attain 10,000 tons. The carbide is sold for $65 per ton of 2000 lbs. at the Works, and the consumption of the product is increasing rapidly, especially for domestic lighting in different rural districts. About 185 men are employed in the different plants.

Cyanamid. "The American Cyanamid Company, located near Niagara Falls, Ont., manufactures calcium cyanamide by the process of Frank and Caro, the nitrogen being obtained by passing air over heated copper, which is then regenerated by natural gas. The power is obtained from the Ontario Power Co. The Company commenced operations in January, 1910, with a 10,000 ton plant. This is at present producing to its full capacity, and a large extension is contemplated. The cyanamide is not sold as such, but is previously mixed with Chili Saltpeter. The whole output is shipped to the United States."[2]

Silicon Carbide and Graphite. "The Norton Company, of Niagara Falls, N. Y., has a plant at Chippewa for the manufacture of crystolon. The latter is a trade name for carbide of silicon. The raw materials used are two different grades of coke (a metallurgical coke with 92 percent or more fixed carbon and 5 percent ash, and a petroleum coke, containing about 91 percent fixed carbon with less than 1 percent ash), a very pure silica sand, and sawdust. Two grades of product are manufactured, green and steel gray. The power is derived from the Ontario

---

[1] S. Dushman, Trans. Am. Electrochem. Soc. *20*, p. 425.

[2] S. Dushman, loc. cit., p. 423.

Power Co., and amounts at present to 2,000 h.p., which is received at 12,000 volts and transformed to 145 volts, after which it passes through induction regulators which buck or boost the voltage to 70 and 215.

The whole of the production, which amounts to over 5 tons per day, is shipped to the Company's main works at Worcester, Mass., where it is manufactured into different abrasive articles."[1]

The International Acheson Graphite Company has also established a small 1000 Kw. plant near Niagara Falls. The number of men employed is about 30, and the output of the plant during 1910 and 1911 has been over 2,000,000 pounds of Acheson graphite in bulk and powder form as well as electrodes.

Ferro-Alloys. The work of the Department of Mines, in connection with electric processes for the production of iron and steel, has had the direct effect of stimulating at least two companies to embark upon the manufacture of ferro-alloys by the electric process.

After the completion, in 1907, of the Government experiments at Sault Ste. Marie, the Lake Superior Power Co. bought the experimental plant from the Government and used it for the manufacture of ferro-nickel pig from pyrrhotite.[2] At the present time it is utilizing the furnace to produce ferro-silicon for its own consumption.[3]

The other company which is engaged in the manufacture of ferro-silicon is the Electro-Metals Co., at Welland. The company owns about 40 acres of land to the south of the town, on the east side of the Welland canal. The iron ore is imported from the United States, and silica in the form of rock or flint is brought from Frontenac or Parry Sound district.[4] The company has four furnaces of 1,000 to 1,500 h.p. each, the daily production being 5 to 8 tons. The power is obtained from the Ontario Power Co. About 115 men are employed, and the product consists of ferro alloys and carbon electrodes for electric furnaces.

[1] S. Dushman, loc. cit., p. 423.

[2] Report 16, p. 93–94. Pring, p. 73–74.

[3] Report 88, p. 68.

[4] O. B. 1910, p. 30. Report 88, p. 68.

Aluminum, etc. The Northern Aluminium Co., a branch of the Aluminium Co. of America, was the first industry to establish itself at Shawinigan Falls. Owing to the necessity of using direct current at low voltage, "it was considered better to generate the power as direct current. The company therefore take their supply of water from one of the penstocks leading from the canal of the Shawinigan Water & Power Co., and are expected to take the capacity of another penstock. The plant covers an area of about 10 acres."[1] The process used is the well-known reduction process of Chas. M. Hall, the alumina being prepared from bauxite in the East St. Louis (Ill.) plant of the parent company. "There are 340 cells in operation, each producing, on an average, 150 pounds of aluminium, 99.4 percent fine, per day."[2] The total capacity of the works is 25 tons of aluminium per day, about 500 men being employed when the plant is running at full capacity.

The Electro-Reduction Company of Buckingham, Que., manufactures phosphorus and ferro-phosphorus from apatite. No details are available as to the nature of the plant.

SUGAR

The annual consumption of sugar in Canada amounts to about 400,000,000 lbs., most of which is imported. The raw sugar comes from the West Indies and is refined at Halifax and Montreal chiefly; the beet sugar factories also carry on the refining business to a certain extent during their slack season. The beet sugar industry is not a very large one in Canada; the difficulty has been, as at other points on this continent, that the labor is scarce and costly, while, as is well known, the cultivation of the beet requires constant care and attention. No statistics are available at present as to the number of men employed or the output of the various plants, but the geographical distribution of the various refineries may be gathered from the list appended.

The Canada Sugar Refining Co., Montreal;
The St Lawrence Sugar Refinery, Ltd., Montreal;
The Acadia Sugar Refining Co., Halifax;

---

[1] Bulletin 24, p. 434.
[2] Bulletin 88, p. 133.

The Dominion Sugar Co., Wallaceburg and Berlin, Ontario;
The Raymond Sugar Co., Raymond, Alberta;
The British Columbia Sugar Refining Co., Vancouver, B. C.

PAINTS AND VARNISHES

The principal manufacturers of Paints and Varnishes are the following companies:

The Sherwin Williams Co., of Canada, Ltd.,
  Head Office—Montreal,
  Works —Montreal, Toronto, Winnipeg, St. Malo;
The Carter White Lead Co., of Canada, Ltd.,
  Head Office—Montreal,
  Works— Montreal;
The Imperial Varnish & Color Co., Ltd.,
  Head Office—Toronto,
  Works—Toronto;
The Brandram-Henderson Co., Ltd.,
  Head Office—Montreal
  Works—Montreal and Halifax, N. S.;
The Martin- Co., Ltd.,
  Head Office—Montreal,
  Works—Montreal;
Moore, Benjamin & Co., Ltd.,
  Head Office and Works—Toronto;
The Canada Paint Co. Ltd.,
  Head Office and Works—Montreal;
The Standard Paint & Varnish Works,
  Head Office and Works—Windsor, Ont.

The total amount of capital invested in this industry is over $10,000,000 and the annual output is approximately $6,000,000. About 800 to 1000 men are employed in the different plants. The standard products are white lead, red lead, litharge, etc., and different lines of paints and varnishes.

SYNOPSIS

John Birkenbine

Philadelphia, Pa.

The production of over 27 million tons of pig-iron, and 26 million tons of steel in the United States in the year 1910, is greater than the annual record of any country; a result which is not accounted for by the number and size of blast furnaces, but rather to the combined efforts of the metallurgist, chemist and engineer.

Seventy-five years ago isolated furnaces smelted iron ore with charcoal and produced a few tons of pig iron per day—the modern furnace, using coke as fuel, has a daily output 100 times as great as its prototype, and uses less fuel per ton of metal made.

Individual iron ore mines produce one million tons or more of ore, and one mine averaged for five consecutive years three million tons annually.

The ore, fuel and flux are handled in quantity by mechanical appliances, and much of the ore is never touched by the hand of man until the finished products pass from mills, nor in the various processes, is the metal flowing from the blast furnaces allowed to become cold.

While the mechanician and the engineer have been responsible for the physical development of the iron and steel industry, the chemist was equally essential, and the laboratory is in demand at all stages of manufacture, from the winning of the ore to the production of multitudinous forms of merchantable iron and steel. Selection of ores, the theory of the smelting process, the composition of metal for specified uses, the utilization of gas and other waste products, the production of ferric alloys, are guided by the chemist.

General descriptions of the early, intermediate and present types of blast furnaces and their equipment illustrate the eras of development, and the conversion of most of the pig iron into steel of definite composition and test, demonstrate that the phenomenal growth is to be mainly credited to theoretical investigation.

The intimate association of chemistry in all departments of iron and steel manufacture has resulted in placing at the head of many important works men who commenced their business life in the laboratory.

WHAT THE STATES ARE DOING TOWARD THE CONSERVATION AND IMPROVEMENT OF SOIL FERTILITY

T. N. Carver

Harvard University, Cambridge, Mass.

Part I

In preparing this paper, the writer has depended for his information upon the various publications of the United States Department of Agriculture, the Bulletins of the experiment stations located in the various states, pamphlets and bulletins issued by the agricultural colleges, the Report of the National Conservation Commission of 1909, supplemented by a somewhat elaborate correspondence with the directors of experiment stations, professors in agricultural colleges, secretaries of state boards of agriculture, and others.

The scope of the inquiry and its subdivisions are indicated in the accompanying chart, and may be easily understood by a brief glance at the headings of the various columns. Though the paper has to do with the work of the various states in preserving the fertility of the soil, and though the International Association of Applied Chemistry is interested primarily in the chemical elements of soil fertility, yet it seems desirable to include in the scope of this inquiry certain enterprises which have to do directly with physical rather than chemical conditions. The reason for this is that under certain conditions the chemical elements of fertility are in the soil, but they are prevented from operating productively by bad physical conditions. Where, for example, the soil is too dry, no amount of chemical fertility, in the absence of water, will enable the soil to produce crops; or where the soil is so wet as to prevent the air from permeating it, or where the land is so stony as to interfere with its cultivation, the presence of sufficient supplies of nitrogen, phosphorous, and potash is of no avail. This, therefore, is my excuse for including in the first part of this paper some account of the activities of the states in improving three classes of physical conditions in the soil, which may be described as too dry, too wet, too stony.

I have been unable to find that any state is exercising itself in any way toward the encouragement of the clearing of stony land. However, it has seemed expedient to include this column in the table merely to show by contrast how much the states are not doing in this important field. It may be said in explanation, however, that there is very little in the way of clearing stones from the land which cannot be done as well or perhaps better by private enterprise than by public enterprise.

Probably no phase of public enterprise has attracted more attention or appealed more strongly to the imagination than the irrigation of the dry lands of the Far West. So far as the writer has been able to learn, however, none of the states, with the possible exception of Utah, is at the present time carrying on any direct work in the field of irrigation. That is to say, none of them is actually building irrigation works under public management except Utah. A letter to the director of the experiment station at Logan states that Utah as a state is using her funds derived from the sale of lands in the construction of some large reservoirs, thus increasing the amount of irrigated lands. This land is again sold, and the money returned to a fund to build still more reservoirs. The larger part, however, of reservoir building is through government agencies (i. e., federal government), or private corporations under the Carey Act. Mr. R. P. Teele, in the Report of the National Conservation Commission (Vol. II, p. 76), states that Colorado and Montana at one time attempted to manage as a public enterprise the building of irrigation works, but in both instances the policy was abandoned.

It appears, therefore, that the greater part of the work of the states in the matter of irrigation has been in the way of encouraging private enterprise. Private enterprise may be encouraged in several ways,—particularly by means of instruction through the experiment stations and agricultural colleges; by total or partial exemption from taxation; or other favorable legislation, such as the formation of irrigation districts under a special law, the lending of the state's credit to districts or private corporations for the purpose of construction. Practically all the experiment stations and agricultural colleges in the arid section have given attention to problems of irrigation, and furnished instruction to farmers and others interested in irrigation enterprises. It may be surprising to some to learn that even in the humid states this subject has received attention. For example, the state of Massachusetts is carrying on experiments in irrigation for the benefit of market gardeners and cranberry growers. So also are Louisiana and South Carolina in the rice industry. So far as I have been able to discover, no state is modifying its tax system in order to favor irrigation enterprises.

There are two leading methods by which states do by favorable legislation encourage these enterprises. The first is through the formation of irrigation districts in sections already settled. In these cases the land owners in a district take the initiative. If a sufficient number desire it, and if the enterprise meets the approval of the state authorities, then the state lends its aid principally in two ways. The first is by making the scheme compulsory upon all land owners within the district. It simply lends its authority as a territorial sovereign, thus preventing a minority of unwilling owners from standing in the way of the project. The state also exercises its taxing power as a territorial sovereign and raises the funds for the carrying on of the enterprise by taxing the land to be benefited. The second characteristic method by which the states encourage irrigation enterprises is by the acceptance of the terms of the Carey Act of 1894, and its later supplementary acts. This applies primarily to land not yet settled or brought under cultivation. In this case the initiative is taken not by the land owners, but by an irrigation company or corporation, which petitions the state for authority to develop an irrigation scheme to water a district which still forms a part of the public domain. If this meets the approval of the state authorities, they in turn petition the federal government to have these lands withdrawn from settlement and turned over to the state under the terms of the Carey Act. The state then lends its further aid and encouragement to the corporation by giving it certain rights of eminent domain in the construction of its dams and ditches, and sometimes by lending its credit, and also by dictating the terms on which water rights are to be sold to settlers after the enterprise is completed. Eight states have accepted the terms of the Carey Act and encouraged irrigation under it. These states are Colorado, Idaho, Montana, Nevada, Oregon, Utah, Washington, and Wyoming. F. H. Newell, in his paper before the National Conservation Commission, stated that up to that time 1,716,424 acres had been approved for construction under this plan.

Though the question of drainage has attracted less public attention and appealed less to the imagination than irrigation, it is probably of even greater importance from the standpoint of national growth and greatness. Estimates differ widely as to the quantity of land which can be irrigated, but the estimates seldom exceed 50,000,000 acres. The area of swamp land which can be drained is somewhat better known, for the simple reason that there are fewer unknown and unknowable factors in the problem. Here the problem is primarily an engineering one, and involves comparatively little guessing at unknowable climatic conditions. And it is estimated that there are 75,000,000 to 80,000,000 acres of swamp land in the United States, and that fully 60,000,000 acres are capable of reclamation through drainage. These lands lie along the South Altantic seaboard, the Gulf coast, and the northern tier of states from Maine to Minnesota.

By an act of Congress passed in 1850, practically all the swamp lands in the public domain were granted to the states on condition that the proceeds of the sale of such lands should be used for reclamation purposes. In drainage enterprises Florida leads all the other states, and Louisiana and North Carolina are second and third. These states are carrying on, under state enterprise, large drainage operations. Massachusetts, Minnesota, and Mississippi are also engaged in minor drainage enterprises.

Here, however, as in the field of irrigation, the greater part of the work of the various states is done in the way of encouraging private enterprise. Nearly all the states in the humid belt give some instruction as to drainage, though in many cases this relates merely to tile drainage and not to the reclamation of swamp lands. Iowa, Illinois, and several other states, for example, are doing a great deal of underdraining, but mainly to improve land already under cultivation. Several states in the arid belt are also encouraging drainage enterprises, not for the purpose primarily of removing surface water but merely for the purpose of preventing the concentration of alkali on the surface. No state, so far as I have been able to discover, has thought of encouraging drainage through a modification of its tax laws. As in irrigation, so in drainage it is probably true that in most of the states a man is fined for showing enterprise, by having his taxes increased as soon as he improves his land.

Other favorable legislation in the matter of drainage seems to be confined to the organization of drainage districts, somewhat similar in principle to the irrigation districts already described. That is, the state lends its authority as a territorial sovereign to compel the owners in a selected district to contribute their share to the expenses of a drainage system, and its taxing power also as a territorial sovereign to collect the funds necessary to pay the expenses. In some cases also it lends its credit to encourage the sale of drainage bonds.

Part II

Coming now to the problem of preserving the actual fertility of the soil, we have first to consider the fact that one of the greatest sources of soil destruction is the washing away of the soil on the steeper slopes in periods of excessive rainfall. There seem to be three characteristic methods of preventing erosion,—namely, forestation; planting of grasses; diking, terracing, etc. It is difficult to find out to just what extent state enterprises in the field of forestation are for the purpose of preventing erosion. In almost every case there seems to be a mixture of motives, the desire to increase the timber supply, to regulate the flow of streams, as well as to prevent soil erosion. I shall assume, however, that wherever there is a state forest reservation the desire to prevent erosion is present, among other motives. Mr. Zon, of the federal Forest Service, states in the Report of the National Conservation Commission that there are in state forest reserves 3,000,000 acres. Mr. Peters, also of the federal Forest Service, in the same Report, states that the total of state land forested is 9,460,622 acres. He names the following states as owning forest land: Arizona, Arkansas, California, Colorado, Florida, Idaho, Maryland, Massachusetts, Michigan, Minnesota, Mississippi, Montana, Nevada, New Jersey, New Mexico, New York, North Carolina, Oklahoma, Oregon, South Dakota, Washington, and Wyoming. More than half the states give instruction through their agricultural colleges in forestry, and thus to that extent at least lend encouragement to private enterprise in the way of forestation. A number of bulletins, particularly in the southern states, have been issued to emphasize the importance of forests on the slopes to prevent erosion.

In the field of forestation alone does it seem to have occurred to the state authorities to lend encouragement by special modifications of the tax laws. According to Fairchild, in the Report of the National Conservation Commission, the following twelve states make special provision in their tax laws for the favoring of forestation and preserving timber lands: Alabama, Connecticut, Iowa, Maine, Massachusetts, Nebraska, New Hampshire, North Dakota, Rhode Island, Vermont, Washington, and Wisconsin. In most of these cases exemptions or rebates are granted to owners of timber lands in consideration of planting, cultivating, growing, or protecting trees, usually in accordance with regulations specified by law. Iowa, for example, encourages forest and fruit tree planting by an arbitrary assessment of $1 per acre on land so planted. New Hampshire grants a rebate of part of the taxes for a period of years.

Other favorable legislation in the matter of forestation usually takes the form of special fire protection, a forestry service with fire patrols, etc. No state, however, has done enough in this direction to accomplish very much. Other forms of state aid are special appropriations for fighting pests, such as the fight against the gypsy and brown-tail moths in Masachusetts and the pine-tree beetle in South Carolina.

Very little has been done in any of the states in the way of planting grasses to prevent erosion. Massachusetts has provided something of this kind to stop the drifting of the sand dunes on Cape Cod. A number of the southern states have spread information as to the value of grasses as a means of holding the soil in place.

If we except the levees along the Mississippi River, which are not so much for the prevention of erosion as for the prevention of overflow, practically nothing has been done by the states to encourage diking and terracing. The agricultural colleges and experiment stations of the southern states have all given out information and conducted demonstrations to show how contour plowing, terracing, etc., may help to keep the soil on hillsides.

Entirely apart from the lack of a sufficient supply of plant food, there are other bad chemical conditions due to the presence of too much of certain chemicals in the soil. Soils of this kind may be grouped under the two general heads of alkali soils and acid soils. Most of the experiment stations and agricultural colleges in the arid states have been grappling with the alkali problem, and conducting experiments to discover the best way of handling it. So far as the writer can find, no state is doing anything else to solve this problem. Most of the older states, particularly on the Atlantic seaboard, are troubled more or less with acidity of the soil. It seems to be a relatively simple problem, and calls for no form of state enterprise except in the way of instruction. Most of the agricultural colleges in this section have been urging the farmers to use more lime, to correct the acidity of the soil. This seems to be about all that the situation calls for.

We now come to the question of the direct preservation and improvement of soil fertility. This is the question which appealed first to our agricultural colleges and experiment stations. Consequently we find that every state has been dealing with this problem, but the universal practice is to lend aid to private enterprise through scientific investigation and instruction. Though most of the agencies carrying on this work owe their initiation to the bounty of the federal government, they have been so long carried on under state management, and most of them have received so much additional support from state funds, that it is entirely proper to classify them under state enterprises.

With the possible exception of the problem of preventing erosion, this is by far the largest problem in the whole field of national conservation. The agricultural soil is so much the greatest natural resource of the nation that no other is even second to it. Inadequately as the soil is now utilized, its annual products exceed in value the combined value of all the mines, oil and gas wells, fisheries, and forests.

As to the inadequacy of our methods of handling the soil, a great deal of sheer nonsense has been uttered by certain apostles of conservation. This may or may not be justifiable in one whose function is to stir up public sentiment rather than to tell the truth. A certain type of windy conservationist has expatiated upon our small product per acre in contrast with the larger product per acre of European countries. The simple fact is, however, that the test of good agriculture is not a large product per acre, but a large product per *man*. And no country in the world can show so large a product per man for its agricultural population as can the United States. It is upon the product per man and not upon the product per acre that the standard of living and the civilization of our rural population depend. Therefore, let it be clearly understood, once and for all, that the only legitimate purpose of soil improvement and conservation is to increase the product per man, and that a larger product per acre is desirable only when it gives us a larger product per man, and is a thing to be shunned as the plague if it is to be secured by those forms of intensive culture which are forced upon overpopulated countries, where labor is abundant and cheap and land scarce and dear. Let us hope as we hope for nothing else in this world that we may preserve, as long as we can, those conditions where men are dear and land cheap, rather than those where land is dear and men are cheap. If we hope for those conditions, we shall stop talking about that kind of intensive culture which prevails in all old and thickly populated countries, where, because of the density of the population, land has become scarce and dear and men abundant and cheap.

It is a natural result, and very much to the credit of our agricultural enterprise, that in a country where land has been cheap and men dear our inventive genius has been exercised in the direction of contriving labor-saving rather than land-saving devices. If we are ever forced, by the opposite set of conditions, to economize land rather than labor, there is little reason to doubt that the same inventiveness and adaptability which has enabled the American farmer to economize labor will then enable him to economize land to the same degree. We shall therefore have our larger product per acre if we are forced to it.

Nor need we assume too easily that the country must be agriculturally self-supporting. In these days of world-wide commerce and cheap transportation there is no special reason, except for the possibility of war, why any particular section of the earth's surface should be self-supporting in an agricultural sense. Neither Manhattan Island, nor Boston Neck, nor Great Britain, nor Belgium is self-supporting in this sense. In fact it will be a wise economy to depend upon foreign territories for certain agricultural products, as our country becomes more densely populated. It happens, for example, that the production of wheat and beef is carried on most economically where land is abundant. These are products which do not respond so well to intensive culture as do some other products; consequently no densely populated country ought to try to produce its own wheat and beef. To do so would be to use land for these crops which might better be used for more productive or more heavy yielding crops. The alarm over the possible decline in our wheat crop is therefore misplaced. It is not a sign of declining agriculture, but a sign of increasing population, making it advantageous to use our lands for heavier yielding crops, depending upon sparsely settled areas beyond our borders for such light yielding crops as wheat and beef.

It is a distinct evidence of the wisdom and sanity of the directors of our experiment stations, and the instructors in our agricultural colleges, that this vast system of agricultural education has not resulted in misguided attempts to gauge our agricultural progress by the product per acre. If that were the test of efficiency of a system of agricultural education, we should make a poor showing indeed. Nor have they regarded it as their mission to try to make the country agriculturally self-supporting, but rather to enable the agricultural population to utilize their labor on their land so as to secure the largest income per man, or per family, and to live upon as high an economic plane as possible. Judged by this standard, our system of agricultural education makes an excellent showing as compared with that of other countries, though there is much to be done yet.

Aside from the purely educational work of the agricultural colleges and experiment stations, a number of states have encouraged the use of commerical fertilizers by laws controlling the advertisement and sale of this form of merchandise. One of the most effective hindrances to the use of fertilizers is the uncertainty of the average farmer as to what he is buying. Any kind of legislation which really prevents fraud in the manufacture and sale of fertilizers, and gives the farmer a reasonable confidence that he is not being swindled by the manufacturers, must therefore be called favorable legislation. If commercial fertilizers can really be standardized by law and sold by grade or standard, it will be the most favorable kind of legislation the state could enact, and would do a great deal toward the improvement of soil fertility.

Illinois has made a generous appropriation, amounting to $65,000 a year, for a soil survey of the state. This survey is being conducted under the efficient direction of Professor Cyril G. Hopkins. It is so significant and so valuable that it has seemed desirable to distinguish it as direct work of the state for the improvement of the soil. Missouri is also doing valuable work along a similar line.

STATES	IMPROVING PHYSICAL CONDITIONS												PRESERVING SOIL FERTILITY																			
	IRRIGATION				DRAINAGE				CLEARING STONES				PREVENTING EROSION												REMOVING or NEUTRALIZING SUPERFLUOUS CHEMICALS(6)				RESTORATION or PRESERVATION of CHEMICAL ELEMENTS of FERTILITY(7)			
													Forestation				Planting Grasses				Diking, Terracing etc.											
		Encouragement Bounty & Enterprise				Encouragement Bounty & Enterprise				Encouragement Bounty & Enterprise				Encouragement Bounty & Enterprise				Encouragement Bounty & Enterprise				Encouragement Bounty & Enterprise				Encouragement Bounty & Enterprise				Encouragement Bounty & Enterprise		
	Direct	Instruction	Total or partial exemption from taxation	Other favorable legislation (1)	Direct	Instruction	Total or partial exemption from taxation	Other favorable legislation (2)	Direct	Instruction	Total or partial exemption from taxation	Other favorable legislation	Direct (3)	Instruction	Total or partial exemption from taxation	Other favorable legislation (5)	Direct	Instruction	Total or partial exemption from taxation	Other favorable legislation	Direct	Instruction	Total or partial exemption from taxation	Other favorable legislation	Direct	Instruction	Total or partial exemption from taxation	Other favorable legislation	Direct	Instruction	Total or partial exemption from taxation	Other favorable legislation
Alabama		Yes				Yes									Yes	Yes		Yes				Yes								Yes		
Arizona		Yes											Yes					Yes								Yes				Yes		
Arkansas								Yes					Yes																	Yes		
California		Yes		Yes		Yes										Yes										Yes				Yes		
Colorado	Yes			Yes										Yes		Yes										Yes				Yes		
Connecticut						Yes		Yes						Yes	Yes	Yes														Yes		Yes
Delaware								Yes																						Yes		
Florida					Yes			Yes																						Yes		
Georgia																														Yes		
Idaho		Yes		Yes																										Yes		
Illinois						Yes										Yes													Yes (8)	Yes		
Indiana						Yes								Yes				Yes												Yes		
Iowa						Yes									Yes															Yes		
Kansas		Yes		Yes		Yes								Yes		Yes		Yes								Yes				Yes		
Kentucky						Yes												Yes												Yes		
Louisiana		Yes			Yes			Yes								Yes														Yes		
Maine													Yes	Yes	Yes	Yes										Yes				Yes		
Maryland								Yes						Yes		Yes														Yes		
Massachusetts		Yes			Yes	Yes		Yes					Yes	Yes	Yes	Yes	Yes													Yes		
Michigan						Yes		Yes					Yes			Yes														Yes		
Minnesota					Yes	Yes							Yes	Yes		Yes														Yes		
Mississippi					Yes	Yes		Yes						Yes								Yes								Yes		
Missouri								Yes																					Yes	Yes		Yes
Montana	Yes			Yes									Yes																	Yes		
Nebraska		Yes													Yes															Yes		
Nevada		Yes		Yes																										Yes		
New Hampshire						Yes							Yes	Yes	Yes	Yes										Yes				Yes		
New Jersey								Yes					Yes	Yes		Yes														Yes		
New Mexico		Yes		Yes																						Yes		Yes		Yes		
New York						Yes							Yes	Yes		Yes														Yes		
North Carolina					Yes			Yes																						Yes		
North Dakota															Yes															Yes		
Ohio						Yes		Yes																						Yes		
Oklahoma		Yes		Yes	Yes																									Yes		
Oregon				Yes												Yes														Yes		
Pennsylvania																Yes														Yes		
Rhode Island						Yes		Yes							Yes															Yes		
South Carolina		Yes				Yes		Yes						Yes		Yes						Yes								Yes		
South Dakota		Yes		Yes		Yes										Yes														Yes		
Tennessee																														Yes		
Texas				Yes		Yes		Yes										Yes				Yes								Yes		Yes
Utah	Yes			Yes																										Yes		
Vermont													Yes	Yes	Yes	Yes														Yes		Yes
Virginia																														Yes		
Washington				Yes											Yes	Yes														Yes		
West Virginia																														Yes		
Wisconsin						Yes		Yes							Yes	Yes														Yes		
Wyoming		Yes		Yes												Yes														Yes		

In this chart the answer "Yes" occurs only where the author has positive information. There are doubtless other cases of state activity, but the author was not able to elicit definite and positive statements covering the points in question.

(1) By the formation of irrigation districts and the acceptance of the Carey Act.

(2) By the formation of drainage districts and the guaranteeing of the bonds of the drainage associations.

(3) State forest reserves and other state owned land on which timber is growing.

(4) In the field of forestry alone has any encouragement been given through exemption from taxation.

(5) Distribution of seeds and nursery stock at cost, fire protection, fire patrol, war against insect pests, etc.

(6) The problem of acidity in the humid belt, and of concentration of alkali in the arid belt.

(7) This is the great field for the work of the experiment stations and agricultural colleges.

(8) Illinois has made a generous appropriation for a soil survey under the competent direction of Professor Cyril G. Hopkins.

THE RESEARCH CORPORATION, AN EXPERIMENT IN PUBLIC ADMINISTRATION OF PATENT RIGHTS

By F. G. Cottrell

San Francisco, California

Some seven years ago the author while working in the University of California on a set of problems in sulphuric acid manufacture came upon certain phenomena which promised to lead to important improvements in the electrostatic collection of smoke and fumes from chemical and metallurgical plants. He was at once confronted by the old dilemma of adjustment between academic and commercial activities, as only through direct construction and study of installations on a commercial scale did it seem possible to develop into full usefulness the inventions involved.

Finally with the help both personal and financial of Prof. Edmond O'Neill of the Chemistry Department and Dr. Harry East Miller and Mr. E. S. Heller, both alumni of this Department of the University, the commercial development of the project was undertaken and patents secured, the understanding among those thus actively concerned being that when the receipts from the business should have repaid the initial investment with reasonable interest at least a considerable portion of the patent rights should be turned over to the University of California or some other public institution to be administered as the nucleus of a fund for the promotion of research, it being also hoped that this might set a precedent and stimulate similar contributions from others.

The business and technical development of the project struggled through and over many difficulties and disappointments for the first few years but with a constantly growing scale of operation and it was not until the fifth year of the work that the latter repaid what the organizers had spent upon it.

It is not the purpose here to enter upon the technical details of the inventions involved as the early history of these was published a year ago[1] and has since been extensively abstracted in other journals.[2] A further supplementary account and discussion was also given at the annual meeting of the American Institute of Mining Engineers last February[3] and two papers on the latest development of the subject are being presented before other sections of this Congress.

Merely as an index to the practical significance which the work has already attained, suffice it to say that installations made under these patents have now been in commercial operation for over five years and the largest of these have been on a scale representing a construction cost of over $100,000 each. The first were in the far West but several are now in operation or under construction in and about New York City.

By the time the work had thus reached a self-supporting basis, its significance was felt to have broadened to a degree which made its control by a local institution such as a single University inexpedient as the fullest success of such a movement is inevitably conditioned upon its being most broadly representative of the common interests of those whose co-operation and support it aspires to secure. Through Director J. A. Holmes of the U. S. Bureau of Mines, who had taken a very helpful interest in the work, it was brought to the attention of the Smithsonian Institution nearly two years ago, the informal discussion which followed resulting last October in a formal offer of the patent rights to the Institution. The only condition qualifying this offer was that these patent rights should be given an adequate business administration and the proceeds be devoted to furthering scientific research.

In December last, after careful consideration and discussion with the prospective donors and under their hearty indorsement, the Board of Regents of the Smithsonian Institution adopted the following resolutions:

---

[1] The Electrical Precipitation of Suspended Particles. Journal of Industrial and Engineering Chemistry, Aug. 1911, Vol. 3, p. 00.

[2] Engineering News, Oct. 26, 1911, pp. 495–498. The Engineering and Mining Journal, Oct. 14, 1911, Vol. 92, pp. 763–764. Mining and Scientific Press, Aug. 26 and Sept. 2, 1911, Vol. 103, pp. 255–258 and 286–289. Rauch und Staub, Apr. 1912, Vol. 2, pp. 187–195.

[3] At the time of going to press this paper had not appeared in the Institute's Bulletin but is expected soon.

> RESOLVED: That the Board of Regents of the Smithsonian Institution do not deem it expedient for the Institution to become the direct owner of the proposed gift of royalty-bearing patents;
>
> RESOLVED FURTHER: That the Board of Regents of the Smithsonian Institution decide that the Institution may properly accept a declaration of trust from the owners of the patents to hold and operate the same in the interests of the Institution, and to pay over to the said Institution the net profits therefrom.

and further authorized its Executive Committee and its Secretary, Dr. Charles D. Walcott, to co-operate with those from whom the offer had come in the organization of either a subsidiary or an independent board of trustees or directors to conduct the business side of the project.

In elaborating this plan, the organizers have tried to study carefully both the economic and academic needs which it was intended to subserve. The following are among the considerations which have perhaps had most to do in determining the form and policy of the new organization as finally constituted.

During the last few years the rapid growth of engineering and technical education, coupled with a general awakening to the commercial importance of research in the industries, has brought about a persistent demand the world over for closer and more effective co-operation between the universities and technical schools on the one hand and the actual industrial plants on the other.

The value to both sides from such co-operation is today generally conceded, but as to the most expedient methods of its accomplishment opinions differ, and we are still in the experimental stage of working out the problem.

One solution which has been extensively applied consists in the universities and schools permitting and even encouraging the members of their teaching staffs to go into private consulting practice. Another form of co-operation is seen in the Industrial Fellowships recently established at several universities, through which their laboratories undertake the investigation of certain problems for individual commercial firms or organizations, the latter bearing the expenses and receiving the first fruits of the investigations, but under restrictions as regards final publication and use, intended to justify the universities or technical schools in taking their part in the work.

While these and similar methods now in use bring about the desired co-operation, it has been felt by some that they are open to the objection of introducing too direct business relations between the academic institutions or the members of their faculties and individual financial interests. As still another alternative, intended particularly to meet to some degree at least this last objection, the Research Corporation has been organized.

Briefly stated, this latter is a board of administration, whose work is to guide the development of such patents as may be turned over to it, and finally market them, the net profits from all such business being devoted to scientific research "by contributing the net earnings of the corporation.. ....to the Smithsonian Institution and such other scientific and educational institutions and societies as the Board of Directors may from time to time select, in order to enable such institutions and societies to conduct such investigations, research and experimentation." Under this system, it will be noticed, a part at least of the financial returns of the scientific investigations of our academic laboratories automatically goes back to them for aiding further investigations.

But this represents only one side of the good which the plan aims to accomplish. Conservation has of late become a word to conjure with, and all manner of economic wastes are very properly receiving a too-long delayed attention. The men in our universities and colleges have been among the first and most effective in promoting the general conservation movement, yet there is what we may term an intellectual by-product of immense importance, a product of their own activities still largely going to waste. This is the mass of scientific facts and principles developed in the course of investigation and instruction which, through lack of the necessary commercial guidance and supervision, never, or only after unnecessary delay, reaches the public at large in the form of useful inventions, and then often through such channels that the original discoverers are quite forgotten.

The Research Corporation was primarily intended to serve the ever growing number of men in academic positions who from time to time in connection with their regular work evolve useful and patentable inventions, and without looking personally for any financial reward would gladly see these further developed for the public good, but are disinclined either to undertake such development themselves or to place the control in the hands of any private interest.

During the process of organization, however, it became evident that the class of donors of patents to the cause would by no means be limited to men in academic positions, but rapidly extended not only to private individuals outside the colleges, but even to large business corporations who often find themselves incidentally developing patents which overrun their own field of activities. Such patents are very apt to get pigeon-holed and come to actually stand in the way of true industrial progress, even though their owners may realize that development and use by others would indirectly benefit themselves. As an official of one of the large electrical companies put it—"Any extension of the use of electricity, or even power in general, is pretty sure eventually to mean more business for us through one department or another."

A procedure adopted in academic and public positions by many men in an attempt to bring various inventions before the public and at the same time prevent private monoply has been to secure patents as matter of record and then throw them open gratis to public use. This procedure received official recognition in the U. S. Patent Act of March 3, 1883, which authorizes the remission of all Patent Office fees to Government officials on patents bearing on their face permission for everyone in the country to use the invention without the payment of any royalty.

Practice has shown, however, that this does not accomplish all that had been hoped for it. A certain minimum amount of protection is usually felt necessary by any manufacturing concern before it will invest in the machinery or other equipment, to say nothing of the advertising, necessary to put a new invention on the market. Thus a number of meritorious patents given to the public absolutely freely by their inventors have never come upon the market chiefly because, "what is everybody's business is nobody's business."

If some of these patents, on the other hand, were placed in the hands of such an organization as the Research Corporation, it could study the situation and arrange licenses under fair terms, so as to justify individual manufacturers undertaking the introduction of the inventions, and at the same time would be accumulating from the royalties funds for further investigations.

As to the details of organization, the Research Corporation was incorporated February 26, 1912, as a stock company under the laws of the state of New York, with its office at 63 Wall St., New York City, its declared purposes being:

(a) To receive by gift and to acquire by purchase or otherwise, inventions, patent rights and letters patent either of the United States or foreign countries, and to hold, manage, use, develop, manufacture, install and operate the same, and to conduct commercial operations under or in connection with the development of such inventions, patent rights and letters patent and to sell, license or otherwise dispose of the same, and to collect royalties thereon, and to experiment with and test the validity and value thereof, and to render the same more available and effective in the useful arts and manufactures and for scientific purposes and otherwise.

(b) To provide means for the advancement and extension of technical and scientific investigation, research and experimentation by contributing the net earnings of the corporation, over and above such sum or sums as may be reserved or retained and held as an endowment fund or working capital, and also such other moneys and property belonging to the corporation as the Board of Directors shall from time to time deem proper, to the Smithsonian Institution, and such other scientific and educational institutions and societies as the Board of Directors may from time to time select in order to enable such institutions and societies to conduct such investigation, Research and experimentation.

(c) To receive, hold and manage, and dispose of such other moneys and property, including the stock of this and of any other corporations, as may, from time to time, be given to or acquired by this corporation in the furtherance of its corporate purposes, and to apply the same and the proceeds or income thereof, to the objects specified in the preceding paragraph.

As practically all technical work under the Corporation's supervision will be done in co-operation with either industrial works on the one side, or school and college laboratories on the other, its expenses will be chiefly administrative, and were estimated for the first year at $10,000, the expectation being that after this it would be self-supporting. As a margin for unforeseen contingencies, the capital was placed at $20,000, divided in 200 shares, of a par value of $100 each, and issued under the condition that "no dividends shall be declared or paid thereon, and the entire net profits earned by said capital stock shall be applied to or expended for the aforesaid purposes." All stock issued is also under an option to the Corporation by which the latter may at any time, through its Board of Directors, repurchase it at par, and the stock cannot be otherwise sold, without first notifying the Board and allowing the latter an opportunity to exercise this option.

Of the total of 200 shares, 101 have thus far been issued and their par value paid into the Corporation's treasury as working capital. This stock is held in lots of from three to ten shares by the following list of stockholders:

Edward D. Adams, of the Deutsches Bank, New York.

Cleveland H. Dodge, of National City Bank and Farmers Loan and Trust Company, New York.

James Douglass, President of Phelphs, Dodge & Co., President of El Paso & S. W. R. R., New York.

T. Coleman duPont, formerly President of the duPont Powder Co., Wilmington, Del.

Frederick A. Goetze, Dean of the Faculty of Applied Science, Columbia University, New York.

Elon Huntington Hooker, President of the Development & Funding Co., New York.

Hennen Jennings, of the Sea Board Air Line.

Charles Kirchhoff, Past President American Institute of Mining Engineers, New York.

Benjamin B. Lawrence, Consulting Mining Engineer, New York.

Arthur D. Little, President American Chemical Society, Boston.

Thomas C. Meadows, Vice-President, International Agricultural Corporation, New York.

H. C. Perkins, President, Oriental Consolidated Mining Co., New York.

Charles A. Stone, of Stone & Webster, Boston.

James J. Storrow, of Lee, Higginson & Co., Bankers, Boston.

Elihu Thomson, of the General Electric Co., Lynn, Mass.

Henry R. Towne, of Yale & Towne, President of the Merchants' Association, New York.

Charles D. Walcott, Secretary of the Smithsonian Institute, Washington, D. C.

The Directors, who need not be stockholders, are 15 in number, seven constituting a quorum, and are elected for a period of three years, one-third going out each year. They in turn elect each year an executive committee of five, of which three constitute a quorum. The present personnel of the administration is as follows:

Officers

Vice President	Charles D. Walcott
Secretary	Lloyd N. Scott
Treasurer	Benjamin B. Lawrence
Assistant Treasurer	Columbia Trust Co.

Directors

(To serve until 1913)

T. Coleman du Pont
Charles A. Stone
Arthur D. Little
Elihu Thomson
M. B. Philip

(To serve until 1914)

Frederick A. Goetze
John B. Pine
Benjamin B. Lawrence
Lloyd N. Scott
Charles D Walcott

(To serve until 1915)

Thomas C. Meadows
Hennen Jennings
Elon H. Hooker
Charles Kirchhoff
James J. Storrow

Executive Committee

Frederick A. Goetze, Chairman

Benjamin B. Lawrence	Elon H. Hooker
Charles D. Walcott	Arthur D. Little

John B. Pine, Counsel
Linn Bradley, Engineer

It is not proposed to fill the offices of President and Manager until the work of the Corporation is well under way and the permanent demands and responsibilities on these officers can be better estimated, their duties devolving in the meantime upon the Vice President, Chairman of the Executive Committee and Engineer.

The present organization is not considered as necessarily permanent in all its details but was deemed the most simple and generally expedient for carrying out the initial stages of this experiment in economics, at least until it should have earned a safe working surplus of its own and demonstrated its ability to produce a substantial permanent revenue. It will then devolve upon the Board of Directors to decide upon a definite policy for the ultimate control of the corporation. This may be done by exercising the option to repurchase all outstanding stock at par and then proceed to redistribute the same, as for example, by turning the whole over to the Smithsonian Institution, or perhaps better still dividing it among a number of universities and similar institutions.

This, of course, does not mean that the particular institutions so selected would thereby acquire any more direct claim on the profits of the corporation than others, since the stock is non-dividend bearing, but merely that they would become trustees responsible for the election of Directors who would give the corporation a business administration, thoroughly practical but conforming to the ideals implied by its objects and associations.

The terms under which each new patent shall be acquired by the Corporation are entirely in the hands of the Board of Directors, but at least for some time to come it is probable that only such patent rights will be primarily considered as are offered freely without restrictions as to mode of administration or obligation of any financial return from the Corporation, as present indications are that the latter will find itself well occupied even by these offers alone.

The Board has authority to purchase patents where this may appear as good business policy, which may quite conceivably occur from time to time in rounding out fields in which it has already embarked. Contracts with owners of patents for administrating the same on a profit sharing basis will probably not be considered, chiefly owing to the unforeseen complications which it is easily possible, not to say certain, that such agreements would eventually lead into as the further developments of different interests began to overlap.

A much simpler, safer and more expedient procedure appears to be for the patentee to retain if he so chooses complete title and control of his patent in certain geographical territory while assigning the same in other territory entirely unencumbered to the Corporation. Any development which the latter can give it will then automatically enhance the value to both.

This procedure is well illustrated in the case of the first patents to come into the possession of the Corporation, viz., those referred to above as initially offered to the Smithsonian Institution itself. The owners of these at the time of their original offer had already spent considerable time and money in their development, but from the outright sale of their foreign rights and the rights of six western states (California, Oregon, Washington, Idaho, Nevada, and Arizona), together with a license for the one industry of Portland Cement manufacture throughout the whole United States, they felt adequately remunerated for their work and financial risks, and were willing to turn over all remaining United States patent rights as a nucleus for the experiment in economics which the Research Corporation represents. Together with this came to the Corporation a 10% interest in the net profits of the parties who purchased the rights for the Western States and for the cement industry, while incidentally growing out of the negotiations on the foreign rights, another set of valuable patents has come to the Corporation from Mr. Erwin Moeller, of Germany, which emphasizes in a most practical way the fact that academic organizations and particularly the Smithsonian Institution are international in spirit, and so recognized by scientific men the world over, presenting at once a nucleus from which may well be developed many activities leading toward world consciousness, co-operation and peace.

The present movement, as stated, had its inception on the far western edge of this continent in very unpretentious beginnings, but has already overrun national borders both in the character of its work and the personnel of its supporters. It is a question which should peculiarly interest this Congress as to how far and in what way international co-operation can best be assured in such activities which from their very nature and aims should from the outset transcend political boundaries and national pride and be treated by one and all from a standpoint as broad as humanity itself. It was with this in mind that the present paper has been presented, not so much as a record of present achievement, as to stimulate discussion and co-operative effort toward ever wider and more effective activities in this most promising field.

WHAT THE GOVERNMENT IS DOING IN FORESTRY

Henry S. Graves

Forest Service, Washington, D.C.

It is a matter of history that in all countries the establishment of forestry has been brought about through the activities of the Government. Generally the first step has been to place the public forest lands under proper management. This has been true of the United States as well as of other countries. For many years far-sighted men have been calling attention to the rapidity with which our forests are being depleted, but very little progress was made in the actual protection of the forests until the United States Government initiated a National forest policy.

The foundation for this was laid by the act, passed in 1891, which authorized the President to set aside as forest reserves portions of the public lands adapted to this purpose. Under the authority of this act, Presidents Harrison and Cleveland set aside some 18 million acres as forest reserves prior to 1897. This action attracted relatively little attention. The forests were in the remote regions of the western mountains, and nothing was done to provide for their administration or protection.

The next step was taken when the Secretary of the Interior, in 1896, called upon the National Academy of Sciences to appoint a commission which should report regarding the condition of the public forests and make recommendations with reference to their management. The Act of June 4, 1897, on which is based the present system of administering the National Forests, was a direct outcome of the recommendations of this Commission. As a result of an earlier preliminary report of the Commission, President Cleveland had set aside by proclamation on February 22, 1897, some 20 million acres of forest reserves. This action was followed by a very vigorous protest from the people of the West who misinterpreted the purpose of the reserves and believed that their establishment meant the withdrawal of the land from all development and use. As soon as it was made plain that the purpose was not to close the reserves to the public but to encourage development along lines which would guarantee the continuance of the resources, the opposition began to decline.

The discussion of the whole subject of National forestry resulting from the opposition to President Cleveland's reserves had a far-reaching educational effect. It may well be said that the modern National Forest movement had its real beginnings at that time. Other reserves were added from time to time, and later they were designated National Forests rather than forest reserves. The greatest impetus to the whole movement was, however, given during the administration of President Roosevelt. In 1898 Gifford Pinchot was appointed Chief of the Division of Forestry in the Department of Agriculture. The educational work resulting from his vigorous activities began a movement for the better handling of our forest resources which soon stirred the country. President Roosevelt took deep interest in the subject and supported the movement with great energy.

The bulk of the public forests have now been included within the National Forests. There are, however, still very large areas which should be added to the Forests. These are chiefly in Oregon, Washington, Idaho, Montana, Colorado, and Wyoming. They are not included in the Forests because in 1907 the power of the President to increase the Forests was limited by a law which provided that in these six States there should be no additions except by act of Congress.

The gross area of National Forests now amounts to about 187 million acres, including about 26 million acres in Alaska. These National Forests have been placed under administration and are being handled along the lines of forestry. Their resources are open to use but under such regulations as are necessary for the protection of the public interests and for the perpetuation of the resources. Thus, mature timber is for sale. It is, however, cut in such a way that a new forest is established as the old is cut.

The National Forests have for many years suffered severely from forest fires. The organized protection given by the Forest Service has resulted in a greatly increased growth of timber. Before the Forests were put under administration the loss by fire and other causes exceeded the growth. The forests were continually going backwards although there was very little cutting done upon them. Under the present management the forests are increasing in their productiveness because the openings which were made by the fires are rapidly being filled up by young growth from natural reproduction and by artificial reforestation. It is estimated that the National Forests contain some 580 billion feet of timber of merchantable size. The actual rate of growth aggregates over 3 billion feet. Many of the large bodies of commercial timber are still at remote points, so that the Government is not yet disposing of anything like as much timber each year as would equal the actual growth of the forest. At the present time about 500 million feet are cut each year, and the sales are increasing at a rapid rate with increased demand.

The most difficult problem which the Forest Service has had to meet in handling the Government Forests has been protection from fire. The National Forests, located as they are in the high, rugged mountains, are still in a state of undeveloped wilderness. There are still in most Forests entirely inadequate means of transportation and communication, and in many cases no roads or trails whatever. The Forest Service had the task of placing this very large area under protection all at once. One of the first problems was the construction of roads, trails, telephone lines, ranger stations, and other improvements necessary for fire prevention. Although the Forests have been under management for only a few years, there have already been constructed 10,000 miles of trails and 7,000 miles of telephone lines, in addition to many other improvements. This, however, is only a beginning. There are still needed 80,000 miles of trails and 45,000 miles of telephone lines to complete the first skeleton system of control for fire prevention. This work is being pushed as vigorously as the appropriations by Congress permit. At the present rate of appropriations it will take about 15 or 16 years to finish this primary system of improvements.

The Forests are thoroughly organized, with forest officers located at convenient points for the transaction of business with forest users and for protection. Great progress has been made in the administration of the forests, although not enough money is available to give them the full protection they should have. There should be a much larger force of patrol men than can now be employed.

On account of the very destructive fires in the past the forest has, in many places, been completely destroyed. The burned areas are often so large that natural reproduction will not take place upon them for a great many years. It is therefore necessary for the Government to restore the forest in these places by artificial means. A very substantial beginning has already been made in this direction, and there is planted each year from 20 to 30 thousand acres.

The other resources of the National Forests are handled along the lines of practical conservation. There is a great deal of grass within the Forest boundaries, in the openings and among the trees. Full use of this forage is being made. It is probable that about 100 million acres produce a certain amount of grass among the trees which is available for grazing purposes. Grazing privileges are granted under regulations which insure the full protection of the forest and at the same time prevent the destruction of the productive capacity of the forest range itself. Before the Forests were placed under administration, the mountain ranges were very much overstocked. This condition has been remedied by regulated grazing. There are over nine million head of stock which are grazed on the National Forests.

The same principles of practical conservation are extended to other resources and provision is made for the utilization of land valuable for purposes other than the production of timber. The lands which are chiefly valuable for agriculture are opened for entry to settlers, and since 1906 over one million acres have been opened in individual tracts to 8,000 settlers.

During the year 1911 there were nearly 6,000 separate timber sales; over 40,000 permits issued for free use of timber by settlers; nearly 30,000 permits issued in connection with grazing privileges; and over 5,000 permits for special uses of various kinds. The special use permits comprise over 100 different uses. There are over 200 different water power permits on National Forests. This indicates that the National Forests are actually being used.

The administration of the National Forests represents a great practical demonstration of conservation. The system has now been established and rapid progress is being made in the work.

In addition to the National Forests which are under the jurisdiction of the Forest Service in the Department of Agriculture, there are public forest lands also comprised within the National Parks. These cover some 5 million acres. Most of the National Parks are in timbered regions. They are being carefully protected and administered with a view to their development as great pleasure resorts. Their administration differs from that of the National Forests in that their primary purpose is for recreation purposes and for the preservation of natural scenery, and it is not designed that their resources should be used commercially. In the National Forests the resources are available for use, although the preservation of areas of special interest is carefully considered.

The Government has further the control of the forest lands owned by the various tribes of Indians. These aggregate some 10 or 15 million acres. The Office of Indian Affairs has recently introduced a forest organization and these lands, or such of them as it is designed to keep in permanent reserves, are being handled under modern methods of forestry.

The Government does not confine its activities in forestry to the management of the public forest lands. It has the task also of developing the science of forestry in this country and promoting its establishment throughout the country. The Government is carrying on very extensive work in scientific research in forestry. It has established at Madison, Wisconsin, a laboratory for the study of problems connected with the utilization of forest products. This is one of the best equipped laboratories of its kind in the world, and the work already done has been of great benefit to the various industries engaged in the manufacture and utilization of wood products.

The application of the principles of forestry to the forests of the United States is new. A great many scientific questions still await solution, particularly those pertaining to the rate of growth of trees, methods of reforestation, and methods of handling the forest in such a way as to secure the greatest possible production of timber and other products from it. Such investigations are conducted not only in connection with the National Forests but also throughout the East. The Government is endeavoring to work out many fundamental problems which will be of assistance to private owners in introducing forestry on their lands.

At present the National Forests are located mostly in the West. In connection with their protection and administration the forest officers have interested a great number of private owners in the protection of their property. At the present time, as a direct result of the activities of the Government, many timberland owners have been introducing modern methods of fire protection, and in some cases are going further in the actual practice of forestry.

In order to reach the forests of the East which are now chiefly in the hands of private individuals, the National Government has initiated a policy of purchasing lands in the eastern mountains whose proper handling is necessary for the protection of navigable streams which rise within these areas. The Weeks Law, passed in 1911, grants authority and money for the purchase of certain lands. It is not expected that all eastern mountain lands can be purchased by the Government; it is expected, however, that there will be secured by purchase very substantial areas here and there throughout the eastern mountains which will serve as centers for the demonstration of forestry. It is believed that the same kind of co-operation can be secured with the eastern timberland owners as has been secured in the West, and in this way through the establishment of limited forests the effect may be very far reaching.

There is still considerable opposition to the National Forest policy in certain quarters. The country as a whole, however, has definitely placed itself on record in favor of the proper handling of our forests. The opposition is primarily from quarters where special interests are to some extent affected by the system. At the present time the forests of the country are being depleted at a rapid rate in spite of the fact that most of the forests owned by the public are now under proper administration. Private timberland owners have only in a few cases introduced the principles of forestry. The actual amount of timber which is used is about three times that produced throughout the country by growth. This condition can not continue. It is a problem of vital importance to the whole nation to stop the destruction of the forests by fires and to see to it that such methods of handling the forests on private as well as on public lands are introduced as will insure the production of a sufficient quantity of wood and timber to meet the requirements of the country, and the protection of the waters which flow from the wooded hills and mountains.

OUR ANTHRACITE COAL SUPPLY AND ITS CONSERVATION

William Griffith and Eli T. Conner
Scranton, Pa., Philadelphia, Pa.

Kinds of Anthracite

An arbitrary division line between Anthracite and Bituminous coal has been adopted by scientists, based upon the relative proportions of the volatile matter and fixed carbon contained in them, which is known as the fuel ratio. Coals in which the volatile matter is one-eighth of the fixed carbon or less, are termed Anthracite in character, while those having a higher proportion of volatile matter have been classified as Bituminous. While this distinction may serve for scientific purposes, it will not answer for the practical, everyday uses of the coal trade and the consumer. A hard and fast adherence to this arbitrary separation as between these coals therefore, cannot be maintained in commerce, because both in Pennsylvania and elsewhere there are coals which fall upon the Bituminous side of the above classification, and yet, are smokeless, have the physical characteristics of Anthracite, and may be prepared in sizes, shipped and sold for domestic purposes as Anthracite coal, and are so considered and classed by the trade and the consumer.

The one great division point between Bituminous and Anthracite coal, so far as the domestic use of the coal is concerned, is the *smoking point.* Consequently, all coals which burn without perceptible smoke should be included, for economic reasons, by the conservationist, under the general term Anthracite. This smoking point in coal is not a fixed line, but varies more or less around 12% of volatile matter in the coal content, and is probably affected to a certain extent by the relative quantity of the other ingredients contained in the coal. Therefore, for the purposes of this article, Anthracite coal will be defined as any mineral coal which will not smoke in a smothered fire.

Anthracite has been derived, through a natural coking process, from Bituminous coal, and on account of the extent or degree to which the metamorphosis has been carried, we recognize different grades of Anthracite, namely: The softer, semi-anthracites, which contain considerable volatile matter; the harder or dry anthracites, which contain a medium quantity; and the very hard, or graphitic anthracites, in which the coking process has continued to the point where some of the carbon has been changed to graphite. The latter have the usual graphitic luster, are difficult to ignite, but when once ignited, burn at a high temperature and require plenty of draft. The "dry" anthracites may be recognized, usually, by their hardness and bright luster. They burn with a hot, slow fire, without flame, and, like the graphitic anthracites, have more or less tendency toward the formation of clinker in the ash, under intense heat. The semi-anthracites, that is, soft or free-burning anthracite, as it is better known to the trade, has a dull luster, and the nearer it approaches to Bituminous coal the duller the luster and the softer it becomes. It also burns with a short blue flame, without smoke. In some of the softer varieties the flame is longer and is tinged with yellow. It requires less draft, and usually burns away to a fine, feathery ash, leaving a few clinkers. As it is softer, it produces more dust in handling, and on this account it is not so much liked by the portion of the coal trade which is accustomed to the harder varieties. By others, however, it is much preferred on account of its free-burning, quick-firing qualities and its light ash.

ANTHRACITE COAL IN THE UNITED STATES OUTSIDE OF PENNSYLVANIA

The great reserve supply from which we annually obtain an increasing quota of the finest domestic coal in the world is the several basins of the Anthracite Coal Fields of Pennsylvania. These have been operated now for about 100 years, and for the major portion of that time it was the only economical occurrence of anthracite coal known in the United States. Therefore, the idea has gone broadcast over the country, and is still prevalent, that there is no anthracite coal in the United States except in Pennsylvania—which is not true, since we find it occurring in considerable quantities not only in Pennsylvania, but in

Rhode Island, Virginia, Arkansas, New Mexico, Colorado, Washington and Alaska. While the quantity of workable anthracite in these various localities is very limited, it is nevertheless of considerable economic value to the country. The occurrences may be briefly described as follows:

Rhode Island contains anthracite coal, but the coking process has continued to the point where the coal is graphitic in nature, and, owing to the difficulty with which it ignites, it has not been extensively used as a fuel. South of the City of Providence a bed of this coal approaching amorphous graphite has been mined for the purpose of manufacturing foundry facings. It is 30 or 40 feet in thickness, very much crushed, and although it will burn, it is of small value as a fuel. But on the Island east of Narragansett Bay, at the town of Portsmouth, the coal has been found in economical condition. It was mined about 1856, and later, through two slopes about 1800 feet in depth, from which 300,000 or more tons of coal were mined and used for fuel, exhausting about 100 acres of the coal land. The beds are several in number, and of economical thickness, though irregular. The coal is dense, hard, and exists in considerable quantity—doubtless several million tons. From the view point of market demands, accessibility and shipping facilities, its location cannot be excelled. The mines have recently been re-opened. Although the coal is difficult to ignite and when the fire is forced produces considerable clinker, nevertheless, if properly prepared for domestic purposes, it forms an acceptable, economical fuel, particularly if mixed with free-burning coal or coke.

In Virginia anthracite coal of a softer variety is found in considerable quantity. One occurrence is in the rocks of the triassic age, not far from Richmond, Virginia. It is reported, however, to be rather pockety and uncertain in disposition, and the production from this region has been very small, but the mines have recently been re-opened for an increased production.

In southwestern Virginia, however, a rather extended anthracite occurrence exists in the sub-carboniferous rocks in Montgomery and Pulaski Counties, and is at present being mined to some extent. Probably one or two thousand tons per year are produced for local consumption and railroad shipment. The outcrop extends with regularity for about 30 miles continuously along the flanks of Brush Mountain and another adjacent location known as Price Mountain, and also at intervals along the same strike, but in much inferior condition, as far northeastward as the Potomac River. There are here probably 30,000,000 tons of economic fuel contained in the seams, the coal from which is now being mined, prepared, shipped, sold and used for anthracite. There are two beds, one six feet thick and the other 2½ feet. The seams occurring in Brush Mountain are so high in volatile matter in certain localities that they are about on the smoking point. In other places certain parts of the seam will not smoke; other benches will smoke slightly. The coal of the Price Mountain locality, however, is entirely smokeless. This coal is prepared through breakers similar to our Pennsylvania anthracite, and although semi-anthracite in character—in fact, approaching closely to the line of Bituminous coal—is nevertheless a very acceptable substitute for Anthracite coal, and will be more and more used for this purpose with the passing years.

Arkansas: The semi-anthracite coals of Arkansas have long been known and have been mined in a small way for many years. Recently, however, the fields have been more rapidly developed and coal breakers constructed and mines developed on a somewhat larger scale. One area of the Arkansas anthracite occurs in a canoe-shaped basin about three miles long and one mile wide, near the town of Russellville, some 75 miles northwest of Little Rock. The bed is three to four feet thick, and is an excellent domestic fuel. There are probably 5,000,000 tons of coal in the basin and it is being operated through two or three shafts and preparation plants.

At Spadra, about 25 miles westward from Russellville, are a number of other mines now operating a softer grade of what is there termed Anthracite coal. This latter also approaches nearly to the line which separates it from Bituminous coal. It is sold throughout Arkansas, Oklahoma, Kansas City and St. Louis. This coal, together with the Pennsylvania and Rhode Island Anthracites, is found in the carboniferous rocks.

Colorado contains perhaps more anthracite coal than any other of the Western States. The greater proportion is located at points which have been out of touch with railroad transportation, except the "Ruby Mines" and the "Crested Butte" mine, the latter being about exhausted. They are located in Gunnison County, west of the central portion of the State, have been in operation for a number of years, and have produced perhaps 75,000 tons of coal per year. The coal is prepared through anthracite breakers similar to those used in Pennsylvania, and the coal is marketed in Denver.

On the Yampa River in Routt County, to the north, there are other anthracite fields covering considerable areas which are likely to be opened as soon as transportation facilities are provided.

The Anthracite coal fields of Colorado and the Rocky Mountain region generally are found in the cretaceous measures, much more recent and younger geologically than our Eastern coals. In these localities volcanic action, resulting in intrusions or dykes of igneous rock, has furnished the heat necessary to change the fuel from Bituminous to Anthracite; and in a few cases where coal beds are found one above the other, some of the beds have been changed to Anthracite by the proximity of the heated rocks, while the other beds, more remote, are still Bituminous in character.

In *New Mexico*, at Los Cerrillos in Santa Fe County, about 50 miles northeast from Albuquerque, anthracite coal has been mined for a number of years. This coal occurs in the recent rocks, similar to the Colorado coals, and has been transformed to anthracite by the heat due to the eruptive sheets near the coal beds. The coal dips from 13° to 16° and is worked by means of a slope. The seam is 3½ to 4 feet thick, and about 500 tons have been produced per day for a number of years. It is marketed along the line of the Santa Fe Railroad and in the cities tributary to it, and in California.

In *Washington* there are two known occurrences of Anthracite coal in the Cascade Mountains, one in Lewis County, near the head of Cowlitz River, south of Mount Rainier. Here a number of seams of anthracite have been found in steep dips of about 60°. Outcrops are said to extend for a number of miles to the southward and northward from the river. The locality is remote from transportation. No attempt has ever been made to exploit the seams, and although samples and analyses of this coal bed appear to prove it of rather good quality, still nothing is known of the characteristics of the seams themselves, and they may not be economically workable.

In the northern foothills of Mount Baker, near the village of Glacier, about 45 miles from Bellingham Bay Harbor, a field of most excellent anthracite coal exists. This small coal field has been but recently discovered and is not yet exploited sufficiently to permit estimates as to quantity. There are apparently several seams of coal of workable thickness covering an area of several square miles. The coal is of excellent quality, a lustrous anthracite, very compact and firm, and altogether a most acceptable quality. It is near to transportation and adjacent to an extended market on the Pacific coast, and will doubtless soon be developed.

Alaska: So far as is now known, there are but two localities in Alaska which are positively known to carry anthracite coal. These are in the two areas of coal known as the Behring River and the Matanuska fields. In addition to the Bituminous coals contained therein there is also a small proportion of anthracite.

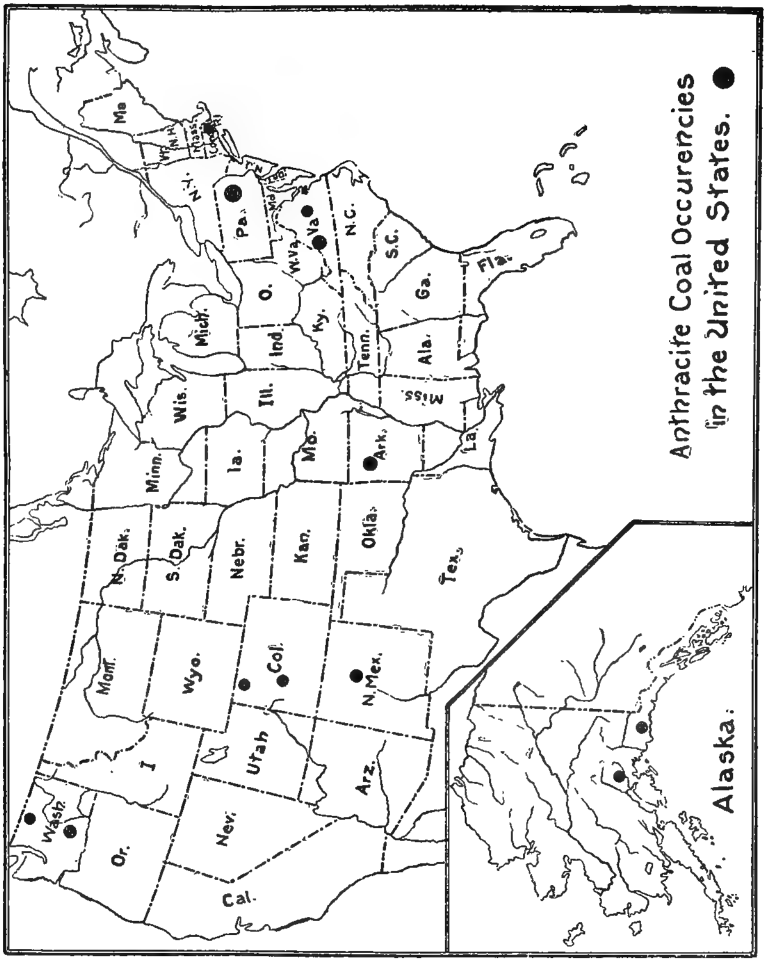
The Behring River field contains considerable high-grade anthracite coal. Like the Colorado coals and other Rocky Mountain anthracites, the proximity of the volcanic rocks has been the cause of the change to anthracite. The coal beds are at all angles of pitch and are of various thicknesses up to 20 feet, but are much crushed and folded; therefore, the quantity of merchantable coal which may be mined from a foot acre of the bed is uncertain, and predictions or estimates as to minable quantity cannot be made with any degree of accuracy.

In the Matanuska coal fields there is but one locality where anthracite coal has been so far discovered. Here a bed of beautiful anthracite about 38 feet in thickness is known, but its extent and prospective value has never been exploited, and as in the Behring River field, no approach to an accurate estimate of quantity can be made. Suffice it to say that the probability is the sum total of the anthracite coal in Alaska which is now available for economical mining is very limited.

A summary of the above Anthracite occurrences outside of Pennsylvania is more concisely set forth by the following tabulation. The areas and quantities therein are merely rough approximations, for the purpose of comparison:

TABLE SHOWING APPROXIMATE QUANTITY OF AVAILABLE ANTHRACITE COAL IN THE UNITED STATES OUTSIDE OF PENNSYLVANIA

State	Approx. Area Workable Acres	Total Produced	Approximate Minable Coal Tons	Approx. Present Annual Production Tons	Approximate Analysis Average					Remarks
					Water	Volatile	Carbon	Ash	Sulphur	
Rhode Island	Perhaps 2 000	300 000	8 000 000	15 000	About 4%	5%	79%	12%		Graphitic
Virginia	25 000	200 000	75 000 000	15 000	0.46 to 0.35	11.35 to 14.31	71.06 to 78.44	16.58 to 6.45	0.55 to 0.45	No smoke Slight smoke
Arkansas	30 000	500 000	100 000 000	120 000	2.07 to 2.11	9.81 to 11.42	78.82 to 77.83	9.30 to 8.64	1.74 to 1.99	Swells in heating
New Mexico	1 000	500 000	3 000 000	50 000	1.5	8.5	82.00	8.00		
Colorado	5 000 to 20 000	2 000 000	25 000 000 to 100 000 000	100 000	.72 to 2.60	7.62 to 4.90	87.51 to 78.20	4 15 to 14.30	Tr. Tr.	Largely Un- developed
Washington	2 000	00	25 000 000	00	3.34	8.44	80.56	6.78	.88	Undeveloped
Alaska	2 000	00	50 000 000	00	7.88 to 5.80	6.15 to 8.87	78.23 to 76.06	7.74 to 9.27	1.36 to 1.08	Undeveloped
Total	76 000 to 87 000	3 500 000	286 000 000 to 361 000 000	300 000						


Anthracite Coal Occurencies in the United States. ●
Alaska.
Me
Vt.
N.H.
Mass.
Conn.
R.I.
N.Y.
N.J.
Del.
Md.
Pa.
Va.
W.Va.
N.C.
S.C.
Ga.
Fla.
O.
Mich.
Ind.
Ky.
Tenn.
Ala.
Miss.
Wis.
Ill.
Ia.
Mo.
Ark.
La.
Minn.
N. Dak.
S. Dak.
Nebr.
Kan.
Okla.
Tex.
Mont.
Wyo.
Col.
N. Mex.
I
Utah
Arz.
Wash.
Or.
Nev.
Cal.

THE PENNSYLVANIA ANTHRACITE

The great reservoir of the Anthracite coal supply of the United States is in the several anthracite coal basins which occupy about 484 square miles in the northeastern part of the State of Pennsylvania, popularly known by the trade as the Wyoming, Lehigh, and Schuylkill regions. As shown on the accompanying map these several basins are long canoe-shaped sinclinals, which contain from five to twenty-five coal beds of varying quality and of workable thickness above the Pottsville conglomerate. The lowest productive beds in the series for the southwestern part of the field are contained in the Pottsville conglomerate and are semi-anthracite in character; but in other portions of the region these inter-conglomerate beds, known as the Lykens Valley seams, are not workable.

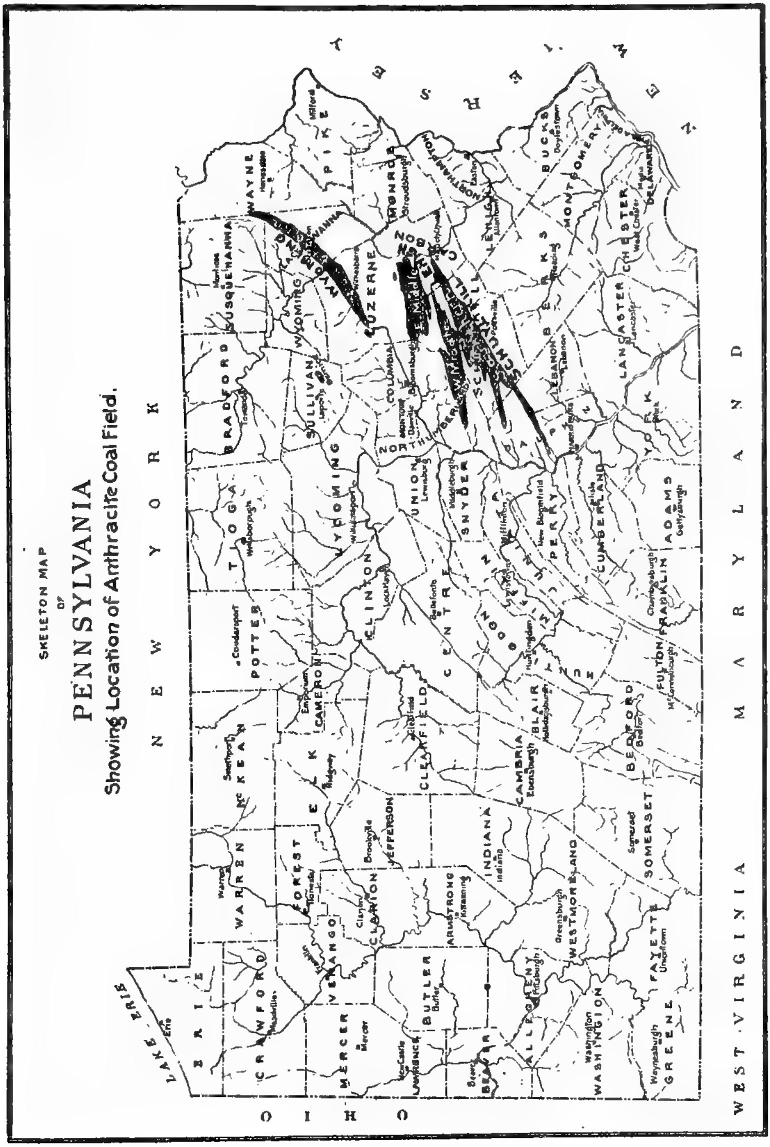
Another small area, known as the Bernice Basin, is in Sullivan County.

Of the workable beds above the conglomerate the lowest is the Buck Mountain or Red Ash bed, which occupies nearly the whole of the above large area. The other overlying beds cover continually diminishing areas from the lowest upward, and are of various thicknesses from two feet to a maximum thickness for the Mammoth bed of about 125 feet.

The coal beds have been very extensively mined and continuously worked for over 100 years. Mining first began at Plymouth, in the Wyoming coal field, in 1807–8, and the trade has continued without interruption since that time, and has increased in a marvelous manner year by year, keeping pace with the rapidly growing domestic demand, the total production of the state in 1910 being 74,717,852 gross tons. In 1911 the output was 81,165,781 gross tons; and for the ten years prior to 1911 the production increased at the rate of about 1,500,000 tons per year.

We present herewith for purpose of comparison, average Analyses of Anthracite Coal from the several regions in Pennsylvania, taken from Reports of the Pennsylvania Geological Survey:

No. of Analysis. Averaged	Name of Coal Bed.	Name of Coal Field.	Chemical Analyses					
			Water.	Volatile Matter.	Fixed Carbon.	Sul-phur.	Ash.	Total
3	Wharton	Eastern Midd'e or	3.713	3.080	86.404	.585	6.218	100
5	Mammoth	Lehigh	4.119	3.084	86.379	.496	5.922	100
3	Primrose	Western Middle or	3.541	3.716	81.590	.499	10.654	100
5	Mammoth	Mahanoy	3.163	3.717	81.143	.899	11.078	100
2	Buck Mountain	Western Middle or	3.042	3.949	82.662	.462	9.885	100
1	Seven Foot	Mahanoy	3.410	3.978	80.868	.512	11.232	100
2	Primrose (F)	Southern or	3.008	4.125	87.982	.506	4.379	100
7	Mammoth	Schuylkill	3.087	4.275	83.813	.641	8.184	100
0	Lykens Valley	Southern or Schuylkill	2.270	8.830	78.831	.676	9.393	100
3	Mammoth or Baltimore	Northern or Wyoming	3.421	4.381	83.268	.727	8.203	100
General average			3.277	4.317	83.294	.600	8.5148	100



SKELETON MAP OF PENNSYLVANIA

Showing Location of Anthracite Coal Field.

Average Specific Gravity

Lehigh Region	1.62	General Average 1.59
Mahanoy Region	1.65	
Schuylkill Region	1.6	
Wyoming and Lackawanna	1.5	

Production, Reserve and Waste

So thoroughly have the fields been exploited during the progress of the mining operations that the area and extent of the various coal beds is known with considerable exactness, and careful estimates have been made of the original contents and future resources of the field. Two very elaborate and painstaking estimates, employing widely differing methods of computation, are particularly worthy of mention, one of which was made in 1893, by Mr. A. D. W. Smith, of Wilkes-Barre, Penn'a, and the other in 1895, by Mr. William Griffith, of Scranton, Penn'a, both of whom, having been engaged upon the Geological Survey of the State in the Anthracite coal fields, possessed exhaustive information as to the geological conditions and the state of the art of mining, preparing and utilizing anthracite coal.

The estimate of Mr. Smith had reference particularly to the original content of the coal field before mining began, and from it as a foundation he computed the quantity of unmined coal remaining at that time. His estimate was published in full in the Report of the Pennsylvania Coal Waste Commission, in May, 1893, and was intended to be liberal according to the mining practice of that day. It included not only the shipments, but the coal burned at the mines, and consumed locally. It included in the Northern field, coal beds 2½ feet in thickness; that is to say, containing 2 feet of clean coal. And in the other fields, beds two feet thick; that is to say, containing 1.44 feet of clean coal and what might be saved from culm piles and mine pillars. Mr. Smith estimated the original content of the Pennsylvania fields before mining began, at 19,500,000,000 long tons, and the available reserve at 6,898,000,000 tons.

The estimate of Mr. Griffith, made in 1905, and published in the Bond Record, New York, was upon an entirely different basis of calculation and for another purpose, being intended as a conservative estimate to ascertain the quantity of export coal which the Anthracite Coal Fields of Pennsylvania might supply for tonnage to the various railroads, and it did not include the coal burned at the mines or consumed locally. Neither did it include any coal in beds less than four feet thick; that is, three feet of clean coal in the Northern field; or three feet thick, that is, 2¼ feet of clean coal, in the other fields. It excluded all coal in culm piles and mine workings. His estimate of available reserve for export was 5,073,786,750 tons.

Re-drawing the latter estimate to conform to the more liberal lines of the former, and combining the two, to construct a new estimate having in view the recent progress toward conservation through modern improvements in the art of mining and using the coal, we have prepared the following tabulation, which we believe accords more closely with latest tendencies of mining practice.

PENNSYLVANIA

Estimate of Anthracite Production and Reserve

1912

Region	Estimator	Area Sq. Miles	Approximate Original Content Long Tons	Approximate Produced to Jan. 1, 1912	Approximate ¼ Wasted and ¾ left in old mines to Jan. 1, 1912	Approximate Reserve Coal in unmined area	Approximate Future Production based on Saving of			Production 1910 Long Tons	Duration of Available Supply at Present Rate of Exhaustion	Estimated Ultimate Waste of Mining
							25% from Old Mines	50% from New Mines	Total available			
Wyoming	Smith	176	5,700,000,000		1,520,000,000							
and	Griffith	176	5,500,000,000		1,871,000,000							
Lackawanna	Av'ge	176	5,600,000,000	1,054,000,000	1,695,500,000	2,850,500,000	423,800,000	1,425,400,000	1,849,200,000	44,600,000	41 Yrs.	2,696,800,000
	Smith	45	1,600,000,000		476,000,000							
Lehigh	Griffith	45	2 100 000 000		569 000 000							
	Av'ge	45	1 850 000 000	312,000,000	523,500,000	523,500,000	130,800,000	502,400,000	633,200,000	10,000,000	63	904,800,000
Schuylkill	Smith	263	12,200,000,000		942,000,000							
and	Griffith	263	11,600,000,000		1,155,000,000							
Mahanoy	Av'ge	263	11,900,000,000	634,000,000	1,048,500,000	10,217,500,000	262,400,000	5,108,200,000	5,375,600,000	20,800,000	260	5,890,400,000
	Smith	484	19,500,000,000		2,938,000,000							
Total	Griffith	484	19,200,000,000		3 595,000,000							
	Av'ge	484	19,350,000,000	2,000,000,000	3 267,500,000	14,082,500,000	817,000,000	7,036,000,000	7,858,000,000	75,400,000	104	9,492,000,000

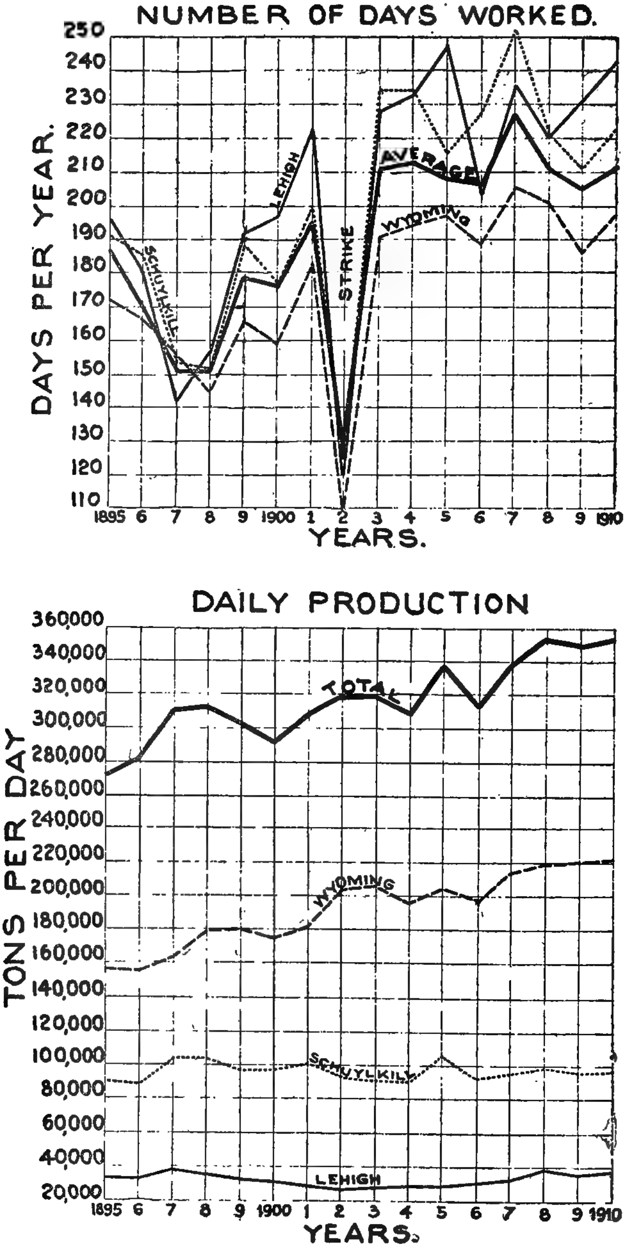
PERCENTAGES OF PRODUCTION AND RESERVE

Region	Percentage of Area	Per Cent. of Original Content	Percentage of Total Production to 1912	Per Cent. of Annual Production	Per Cent. of Available Reserve	Per Cent. of Total Reserve
Wyoming	36.3	28.4	52.2	59.0	23.5	25.0
Lehigh	9.3	9.6	15.6	13.2	8.0	8.5
Schuylkill	54.4	62.0	32.2	27.8	68.5	66.5

The Duration or Life of the Coal Supply

It is impossible to predict with any approach to accuracy, the duration or life of the supply of anthracite coal in the United States, because there are so many unknown quantities entering into the proposition. It would only be remotely approximate to divide the annual rate of exhaustion into the available supply as we have above tabulated it, because we know the production will continue to increase until it reaches a maximum, and then will gradually decrease until the supply is exhausted. At the present rate of mining, the available coal of Pennsylvania would last about 104 years. But our methods of mining are likely to be very much improved in the future, and the results of new discoveries or inventions may change our methods of utilizing it; all of which would tend to conservation and extend the duration of the supply. In fact, during the past ten years marked advance has been made along these lines, and we may expect it to continue in the future. While the Anthracite fields outside of Pennsylvania are important, their tonnage is so limited that the coal from these fields will in all probability be exhausted long before the supply of the Pennsylvania region.

If we analyze the production of anthracite in Pennsylvania by dividing it into its two factors—the number of days worked and the daily production—we will find, as illustrated in the accompanying diagrams, that the principal increase in daily production has come from the Wyoming region, which contains only 33.5 per cent. of the total available reserve. We also note that the



ANALYSES OF
ANTHRACITE PRODUCTION.

average increase in the daily production of the State is nearly parallel with the average increase of the daily production in the Wyoming region, and that the Schuylkill and Lehigh regions have remained approximately constant in daily production for fifteen years. It would seem, therefore, that the maximum tonnage of Pennsylvania soon will be reached, viz., when the Wyoming region ceases to increase its daily production, because the average number of days worked per year in each of these regions has been approximately constant for seven years, and has probably already reached its maximum.

PHYSICAL CONDITIONS INFLUENCING THE MINING OPERATIONS

As such a large percentage of the Anthracite production of the United States is mined in Pennsylvania, the methods of mining and the results attained there can be taken as a fair sample of the production of similar structural and geologic deposits elsewhere in the country; as in the main, Pennsylvania practice is generally followed in other fields.

The large percentage of waste as indicated in the preceding chapter and illustrated by diagram and tables, has always been a subject of great concern to broad-minded, far-sighted mining men, and much thought has been given to the subject of reducing the losses in mining and preparation. This subject was gone into carefully, as referred to in a preceding chapter, by the Coal Waste Commission of the State of Pennsylvania, of which the late Eckley B. Coxe was a member. Mr. Coxe was one of the foremost operators in the Anthracite region, and was a large owner of anthracite coal lands, so that he was directly interested in securing maximum yields from his own properties. The estimate of 50% actual loss of the original content, as shown by our tables, is, under existing methods of mining, about what is at present being attained, taking the Anthracite region as a whole.

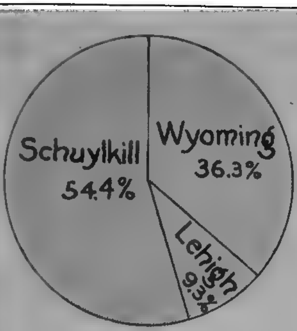
This very great loss is due to several causes. The Anthracite region is divided into several fields, due to geographical location and also to the widely varying character of the geological formation. These several regions are shown on the map accompanying the article.

The Northern Anthracite Field extending from Forest City in Susquehanna County to Shickshinny, in Luzerne County, a distance of about 55 miles, by about six miles in width at the widest point, is so laid down that the measures are comparatively flat, as is indicated by four cross-sections illustrating this article.

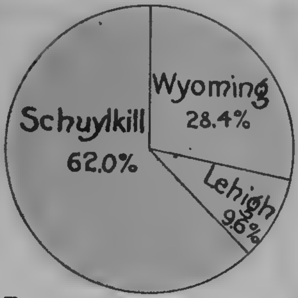
Almost without exception, the room and pillar method of mining has from the beginning, been followed in the Anthracite field. In the earlier days it was found that about one-third of the coal left in the form of pillars was sufficient for roof support, and this proportion ruled to a very great extent, and in some mines is still adhered to. It is a well-known fact that the relative proportion of pillar coal that should be left for the support of varying thicknesses of overburden, has not been definitely determined, although some interesting and valuable experiments to determine the crushing strength of coal have been conducted by engineers of eminence; still the conclusions they have reached are far from final, because each coal bed has peculiarities of its own, which offset its crushing strength, and because the character of the overlying measures varies greatly. No hard and fast rule can be laid down to determine the percentage of pillar coal which should be left in, but each property, and even each portion of any particular tract of land, must be considered entirely by itself in the determination of this point.

To illustrate the room and pillar method of mining, which generally prevails throughout the Anthracite field, there is incorporated with this paper a number of illustrations taken from the Twenty-second Annual Report of the United States Geological Survey, which speak for themselves.

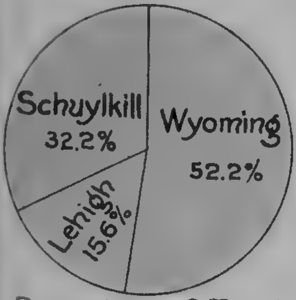
In the early mining in the Northern Anthracite field the developments were made in the middle series of coal beds, known in descending sequence as the Diamond, Rock, Big or Fourteen Foot, New County, and Clark. These beds can be identified on the cross-sections accompanying this article, from which it will be noted that the names differ East and West of Scranton. At Wilkes-Barre the "Big Bed" is known as "the Baltimore," while at Olyphant and eastward to Forest City, it is known as the "Grassy Island."



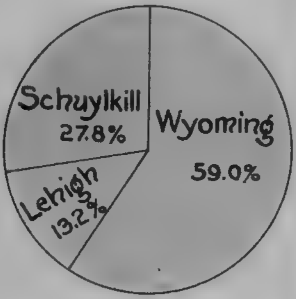
Percentage of Area.



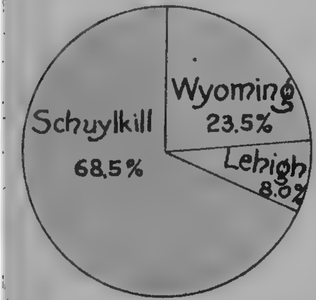
Percentage of Original Content.



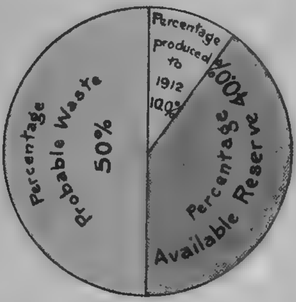
Percentage of Total Production to 1912.



Percentage of Annual Production 1910.

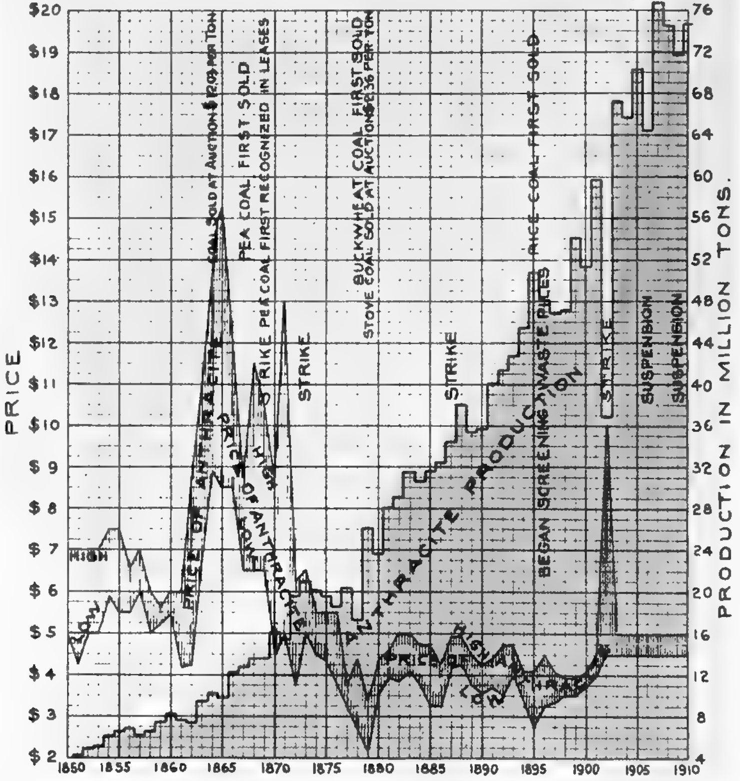


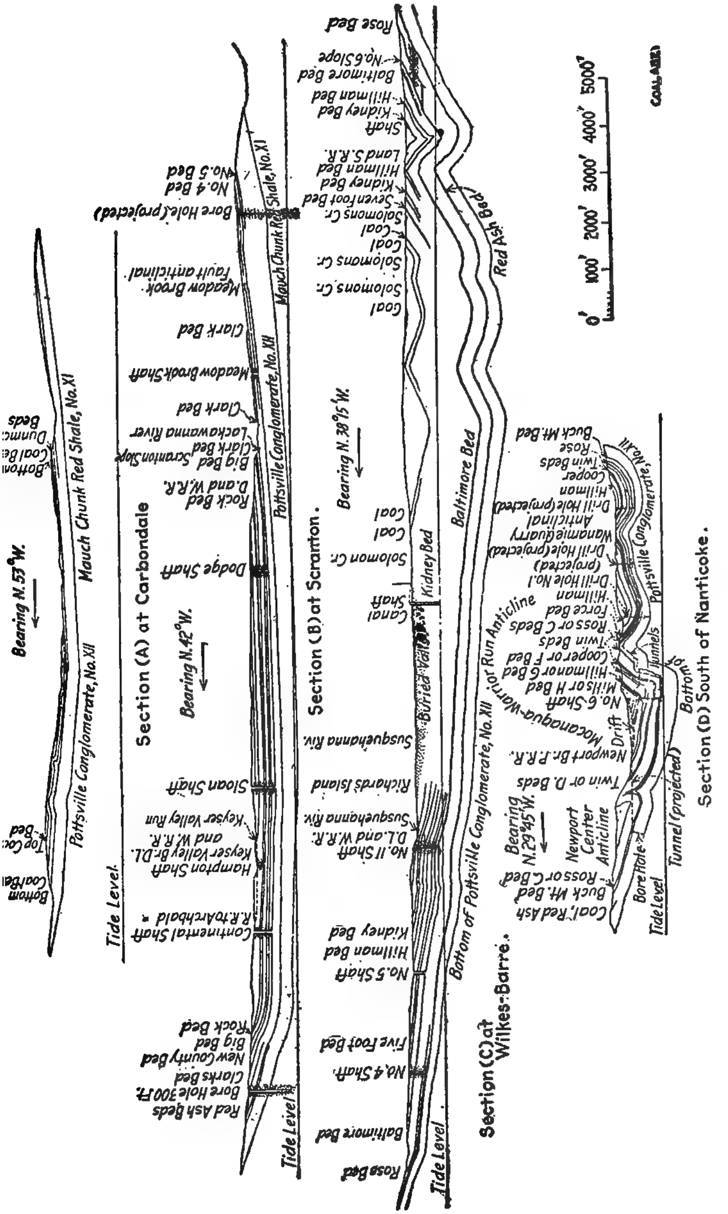
Percentage of Available Reserve.



Percentage of Conservation.

Diagram showing Highest and Lowest Wholesale Price of Anthracite Stove Coal at New York, and Annual Production of Anthracite Coal for Sixty Years.



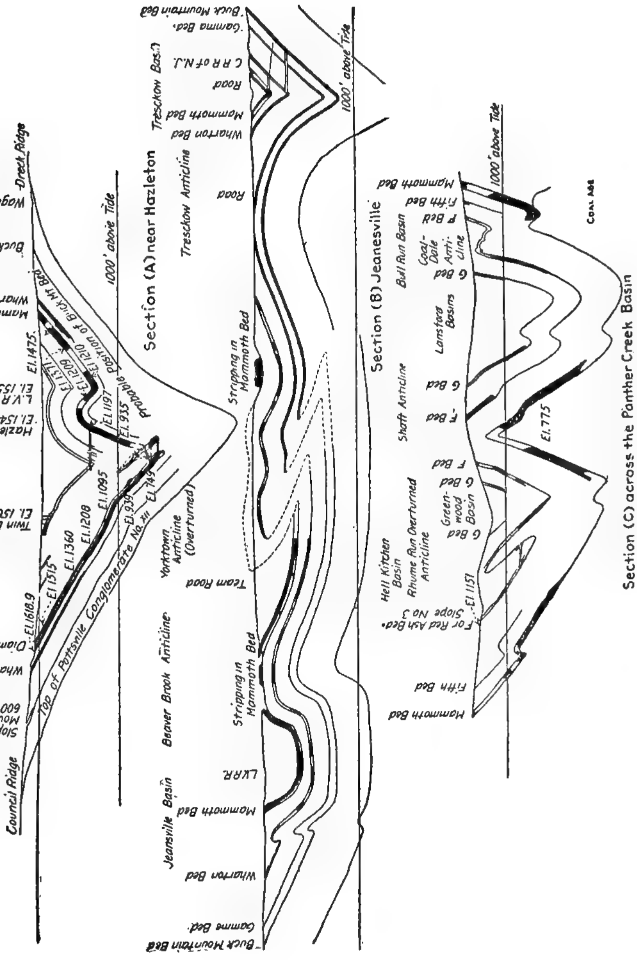


CROSS-SECTIONS OF NORTHERN ANTHRACITE FIELD

In the earlier days of mining it frequently happened that but one or two benches of the bed developed were considered marketable, and consequently the other benches were left in place or broken up and thrown into the gobs. This resulted in the loss of a large quantity of coal, much of which has not, up to the present time, been recovered, and large proportions of these so-called defective benches will never be reclaimed. It will be noted that the five beds of coal above referred to are comparatively thick and relatively close together. It is no uncommon thing to find these five beds aggregating 50 to 55 feet in thickness and included within an interval of 150 to 175 feet.

In the earlier days of the industry, almost without exception throughout the Northern field no attempt was made to lay off the mine workings so as to bring pillars in lower beds under pillars in the beds immediately overlying. The result of this failure to columnize pillars made a very insecure, honey-combed condition, and frequently brought about extensive squeezes that have closed up large areas of the mine workings, practically destroying the remaining pillar coal. A particular instance of the effect of such mining has recently been investigated by the writers, where it was found that, due to the causes above-mentioned, 46% of the original content of minable coal has been practically irretrievably lost. In recent years greater care has been exercised in the columnization of pillars, and a large ultimate recovery can reasonably be expected; but there are enormous areas still standing open where thirty to forty per cent. of the original content remains in pillars, but which cannot, under existing conditions—and particularly on account of the lack of columnization of pillars,—be recovered excepting by a systematic adoption of the flushing or silting of mine openings, advocated by the authors in their Report on Mining Conditions Under the City of Scranton (U. S. Bureau of Mines, Bulletin No. 25). Even where surface support is necessary, we believe the ultimate recovery of the large amount of pillar coal will—if not at present, certainly in the future—justify the expense of adopting the flushing system.

One of the principal reasons for the unsystematic methods of mining in the Anthracite Region, has been that most of the early developments particularly in the Schuylkill fields were

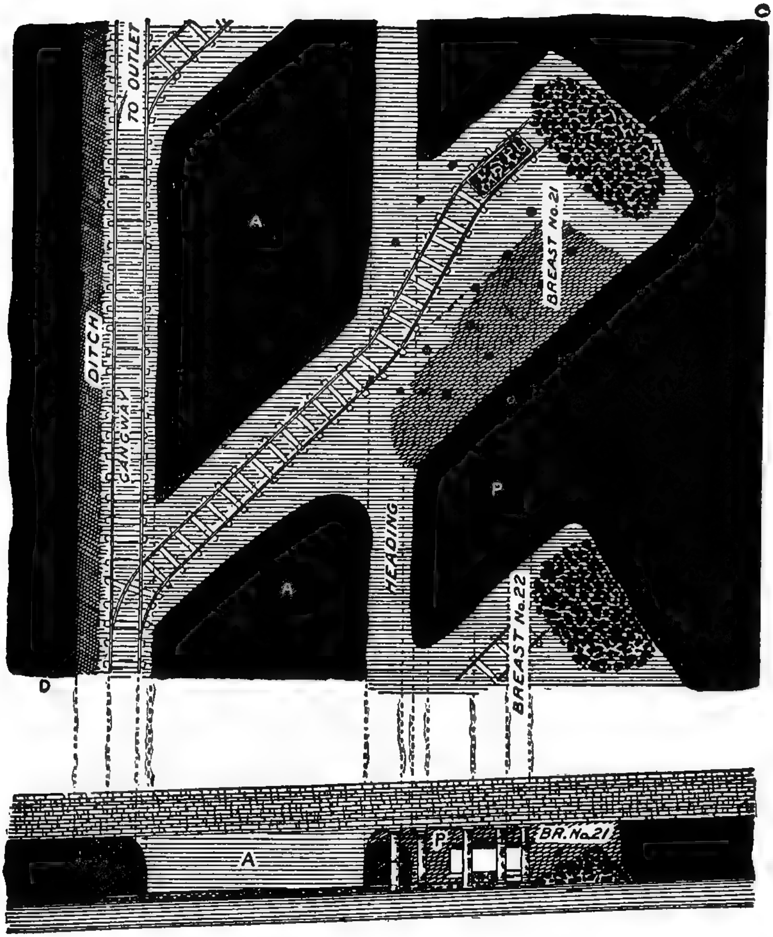


COAL BASINS IN THE EASTERN MIDDLE ANTHRACITE FIELD made by individual operators holding the properties under *comparatively short-term leases*, which carried burdensome minimum royalties, and thus compelled the operator, in order to retire his capital and make a reasonable profit during the term of his lease, to *take only the cream of the property*, oftentimes to the *great detriment of the remaining mineral.* During the past twenty years most of the individual operations throughout the Anthracite regions have come into the possession of the eight railway corporations engaged in the transportation of Anthracite coal to market. These Companies have generally adopted more scientific and systematic methods of mining, and consequently reduced the waste from the causes above-mentioned.

Another fruitful source of waste in mining anthracite in the Northern field is the shooting of the coal off the solid, which has always been the prevailing method of breaking down the coal. In recent years the great improvements in mining machines, and their extensive adoption for mining bituminous coal of all degrees of hardness has, we believe, resulted in the development of machines suitable for undercutting anthracite coal. Some experiments have been conducted with machines of several types, in the Anthracite field, and as far as the mechanical apparatus is concerned, reasonable success has been attained. If this method is more generally adopted for mining thin seams of coal on comparatively flat pitches, it will, we believe, result in saving a large quantity of first-class fuel which has heretofore been blown into the gobs and pulverized into culm.

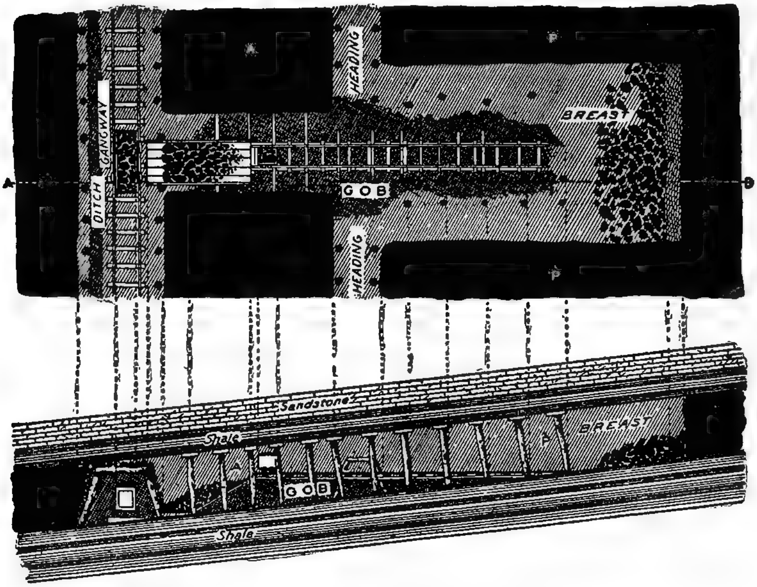
While some experiments have been tried in the Anthracite field of mining thin seams on the "long wall" method, it has never been adhered to with enough persistence to make it a success. The writers are quite satisfied that if this system—which is well known in England and on the continent of Europe—were more generally adopted in America, particularly for the mining of thin seams, decidedly beneficial results would accrue, both in the matter of cost of production and in the increased yield per foot acre of the properties worked over.

The Eastern Middle, or Lehigh Region, greatly differs from the Northern Anthracite field, due to the extreme distortion of the measures. This is well illustrated by the three cross-

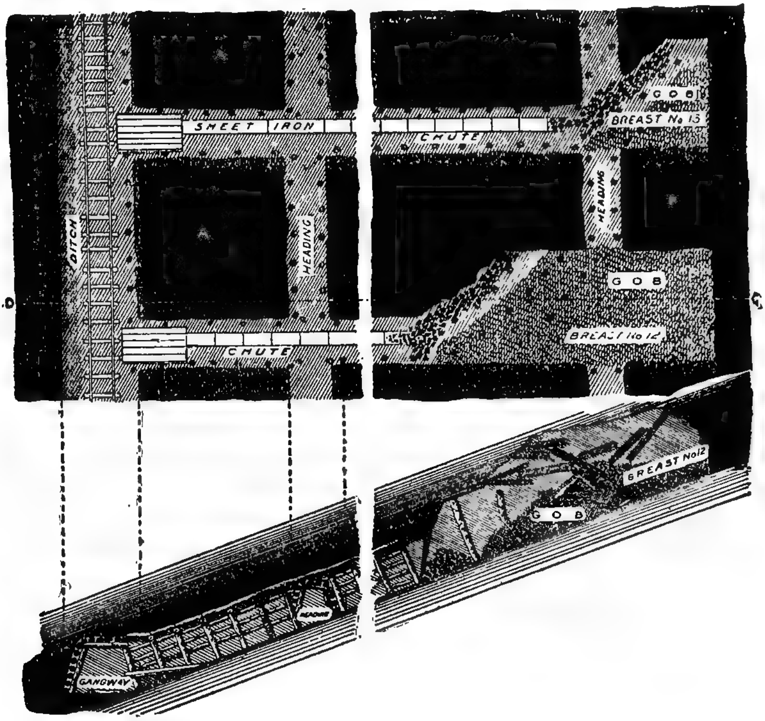


Wagon Breast, Anthracite Region, Under 10 Deg. of Pitch sections accompanying this paper. It will be noted that the main basins in the Lehigh region are deep and distorted, causing excessive pitches; consequently the methods of attack, development and operation must differ widely from those in the Northern Anthracite field.

The principal seam of coal found in the Lehigh region, as elsewhere, is the great Mammoth Bed, which corresponds to the Baltimore seam in the Northern field. This bed, in the Lehigh region varies from 24 to 50 feet in thickness, the average being about 30 feet. Most of the early mine development was made on the Mammoth seam. The methods of development and mining that were inaugurated many years ago, have been continued with comparatively slight changes. These methods are well illustrated by the accompanying cuts, which are also taken from the Twenty-second Annual Report of the United States Geological Survey. These cuts illustrate gangway, airway and

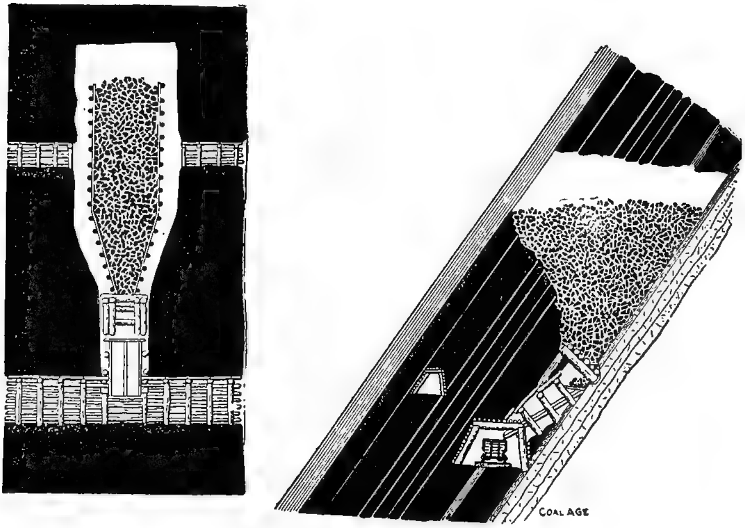


BUGGY BREAST, ANTHRACITE REGION. ON A 10- TO 18-DEG. PITCH chamber workings in thick and thin seams on steep pitches. It will be noted that where the chambers are worked "full," the entire content of the bed, whatever it may be, together with any "slab," "clod," or loose "top rock," must be drawn out of the chute, at the bottom of the chamber, into the mine car, as there is very little opportunity to separate the impurities from the good coal, in the mine. This is not an unmixed evil, as it avoids the great waste referred to in the Northern Anthracite field, throwing into the gob doubtful and off-color benches of coal which if sent outside to the breaker—as is the case where coal is loaded from running chutes—can be inspected, and some part, at least, of the doubtful coal saved for the market. In other



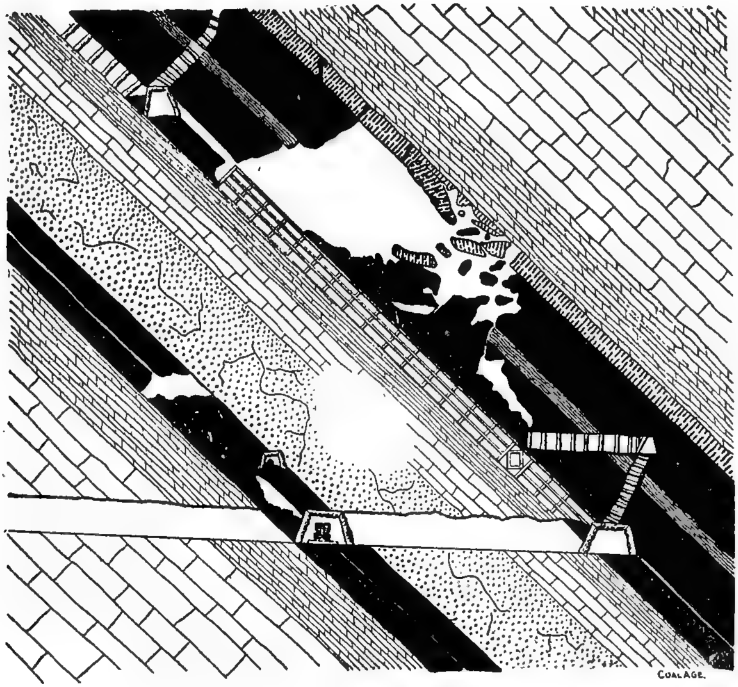
Sheet-iron Chute Breast, Having a Pitch of from 81 to 30 Degrees words, it is not left to the judgment of the individual miner or his laborer to determine what is or what is not marketable coal.

In driving the chutes and chambers, as shown by the cuts referred to, the coal is shot off the solid; but in the Mammoth and other seams it frequently happens that after the chamber has been developed so that the whole seam is cut from floor to roof, it becomes impossible to control the chamber, by reason of the coal "running." When this happens, the miner continues to draw coal out of the chute so long as it will "run." Usually, when one or more chambers break loose in this manner, not only the coal directly in line with the chutes, but also the pillars between adjoining chambers run out, permitting the roof rock to come down. This may, perhaps, occur before all of the solid coal has been recovered. There is no possible way of ascertaining whether or not all of the coal that should come out of a given chute or series of chutes has been recovered, consequently it is necessary to handle the rock that comes when a fall occurs, until the foreman feels convinced that no more coal can be



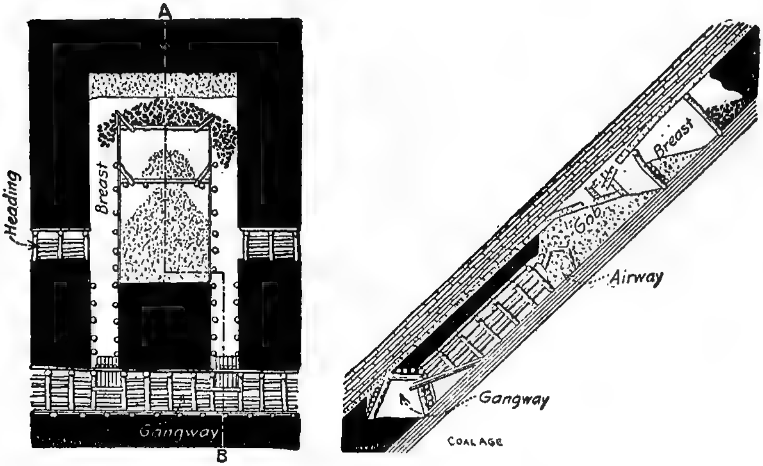
HEAVILY PITCHING BREASTS ON MAMMOTH BED HAZELTON profitably recovered from that chute. In this way enormous quantities of rock are loaded in the mine cars, transported to daylight and dumped on the waste bank.

It is well known that this method of mining very thick beds of coal standing on steep pitches oftentimes results in the recovery of a lamentably small percentage of the original content. Earnest thought and effort have been put forth by able managers to devise better methods of winning these thick beds of coal, but very little change resulting in improved recovery has been made since the early days.



METHOD OF WORKING CONTIGUOUS SEAM THROUGH HORIZONTAL ROCK TUNNEL

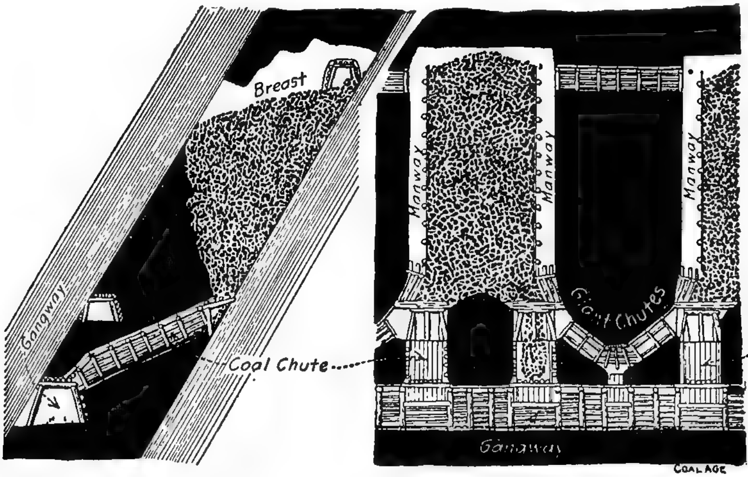
American engineers have been much interested in reports of the successful mining—under the quite different economic conditions which there exist—of thick beds of coal in Europe by what is known as the "slicing method," by which the coal is extracted in slices from the bottom upward, each slice being about 6 to 8 feet thick, and the space from which it is removed being filled with flushed sand or other material before the next slice is extracted. This operation is reported to result in the recovery of practically all the coal, with comparatively slight subsidence of the overlying rock. As a report is shortly to be made on this subject by a Commission recently sent to Europe by the Mining Bureau of the United States Government, no further description of it is necessary here. The forthcoming report will be of great interest to engineers familiar with the methods pursued in mining thick and steep beds in the Pennsylvania Anthracite field.



Method of Working Pitching Coal with Extraction of Refuse

The loss of coal in the Mammoth seam is not the only damage done, as in most cases in the earlier days of the industry no attention was paid to thin and so-called inferior seams of coal overlying the Mammoth, which in many instances have been practically destroyed by the dropping of the underlying strata, due to caving of openings in the Mammoth bed. This destruction of overlying beds was of course, more pronounced years ago than in recent years, because more attention has been given to the conservation of the marketable coal in all beds, even in those as thin as thirty inches.

It will be noted by the cross-sections that there are many instances where the beds of coal come close to the surface at the "spoon" ends of basins, the marginal outcrops and on the crests of anticlinals. In such cases it has been found profitable to strip off the overlying earth and rock, exposing the seam of coal which can then be quarried in open-cut mining. It was formerly the opinion of engineers and operators that one foot of overburden could be removed with profit to effect a recovery of one foot in vertical thickness of coal seam, even though the coal bed had been partially mined by underground methods. This relative proportion has been greatly changed during the past ten or fifteen years, until as much as three feet of overburden, sixty per cent. of which is rock, has been removed for the recovery of one vertical foot of coal bed.



COAL AGE

DOUBLE CHUTE BREASTS, ANTHRACITE REGION

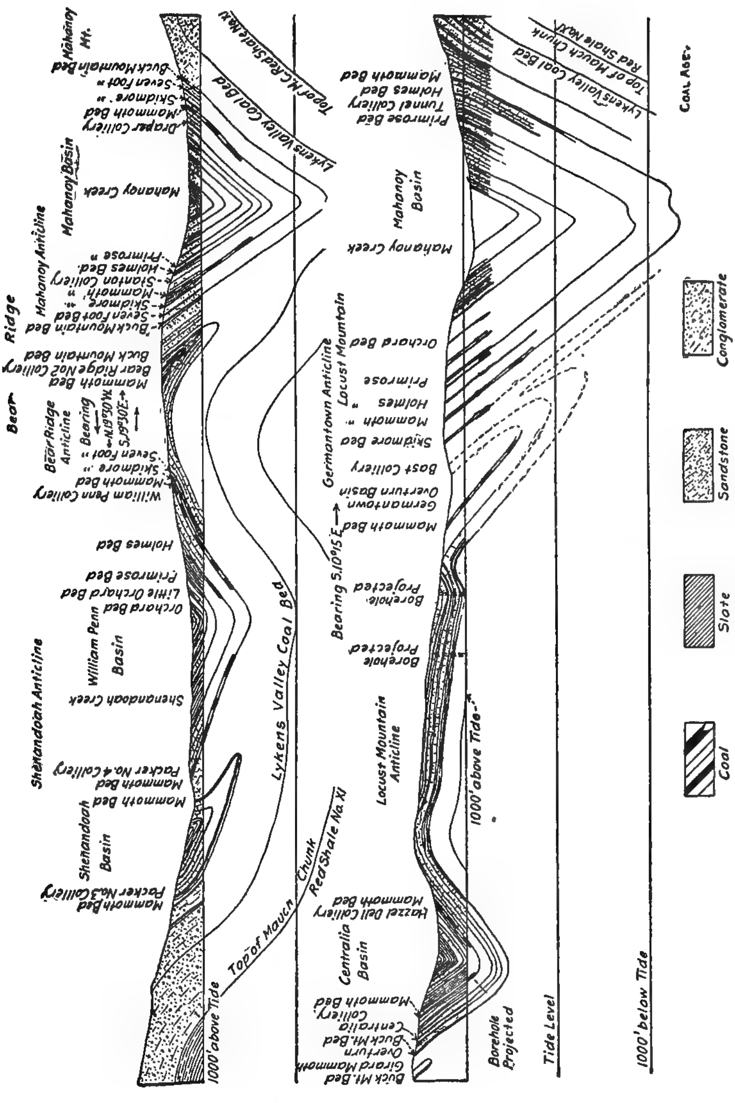
On large operations the cost of this stripping work has been done for 18¢ per cubic yard of earth, and 35 to 40¢ per cubic yard of rock. While stripping means a large outlay before much return can be secured, it permits the recovery of all the coal, with cheap methods of mining and handling.

The early developments in the Lehigh, Western Middle, and Southern fields were by sinking slopes from the outcrop, following the coal bed to the true dip. These openings were generally successful until four or five lifts, about 500 feet apart, on the pitch of the seam, had been turned. By the time the fourth or fifth lift was opened, in many cases the cost of maintenance of the slopes and several landings was and is very great. In recent years important developments have been made by sinking vertical shafts in the centers of the basins with the long axes of the shafts parellel to the axes of the cynclines. From these shafts levels are turned in rock on both sides. These levels are placed so as to intersect the old levels formerly driven from the slopes, and are generally about 400 feet vertically apart. The geologic and structural conditions in the Western Middle and Southern Anthracite fields are similar to those in the Lehigh region.

It is no uncommon thing to find the Mammoth seam from 60 to 150 feet thick. This is particularly the case in portions of what is known as the Panther Creek Basin, being the eastern extremity of the great Pottsville Basin, which extends from the Lehigh River at Mauch Chunk almost to the Susquehanna River at Dauphin—nearly 70 miles.

A cross-section showing the Southern field at Pottsville is incorporated, from which it will be noted that there are a large number of beds of coal greatly distorted—in many places overturned. This distortion has effected the hardness of the coal so that in nearly all of the operations in the Southern field very great waste occurs on account of the friability of the product going to the breakers. There are many instances where over 50% of the raw product reaching the breaker is waste, either in the form of rock, slate, bone or culm.

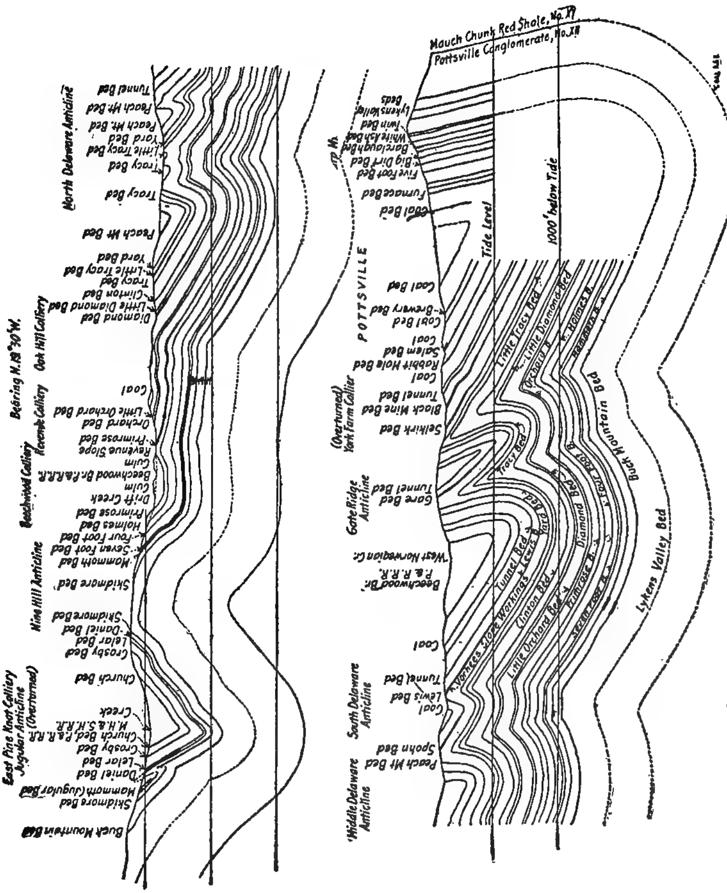
The method of preparation of Anthracite coal is by passing it over screens with meshes of varying sizes to separate the coal into eight sizes, known in the market as Broken, Egg, Stove, Chestnut, Pea, Buckwheat, and Buckwheat Nos. 2 and 3. The larger lumps of run-of-mine coal are passed through toothed rolls, which break it down to the sizes mentioned. This process



CROSS-SECTION WESTERN-MIDDLE ANTHRACITE COAL BASIN necessarily makes greater or less dust, and particles of coal smaller than that which will pass over a 3-32 inch round mesh. In all the Anthractie fields, but to a greater extent in the southern fields, a large amount of good coal is wasted in this dust, which is known as culm. Efforts have been made to develop a process for burning pulverized anthracite coal in the form of a jet blown into the fire box, but this has not yet been successfully accomplished on a commercial basis. It has been found feasible to burn the dust, but one of the difficulties experienced is to construct a fire box that will stand the intense heat of this dust under combustion. The writers are of the belief that this problem will soon be solved. Briquetting has been experimented with, and worked out successfully at two or three plants, which are now producing anthracite briquettes on a commercial and profitable basis, but not in a very large quantity. Efforts are being made to store the surplus dust at some of the mines in such manner that when a market may be developed for it either as dust or in the form of briquettes, the dust can be recovered. *This, however, is not being done* to as great an extent as it should. In many cases the mine operators are washing the culm into the mines and filling up old chambers, which is beneficial for support of overburden, but, we think, an economic mistake, inasmuch as this culm will probably not hereafter be recoverable. We are firm advocates of the flushing or silting system, but think only waste and otherwise worthless material should be used for this purpose.

Mention has been made of the eight sizes of anthracite coal. This sizing has been the result of various compromises in the past, and it is not necessary that the coal, to burn successfully, should be divided into as many separate sizes as now prevail. Recent attempts have been made to reduce the number of sizes, but the various interests were unable to agree on this point. If two or three sizes could be eliminated it would result in conservation, as the more sizes there are, the greater the proportion of breakage and loss, occasioned by the handling and re-handling of anthracite coal.

While the losses mentioned due to sizing and handling of the coal are, in the aggregate, large, they are insignificant in com-



CROSS-SECTION OF SOUTHERN ANTHRACITE COAL BASIN AT POTTSVILLE

(The lower section is a continuation of the upper) parison with the enormous waste underground, particularly in the great Mammoth seam. Constant effort is being put forth by progressive engineers to reduce the losses due to the present methods of mining, and some of the Companies largely interested in the Mammoth seam sent engineers with the representatives of the United States Bureau of Mines, to Europe to study methods of mining there and to profit by any improvements that may have been developed. The reports of this Board of Engineers have not yet been made available to the general public, but we are informed that while European practice is in some particulars in advance of ours, it is not materially so, under similar conditions. We believe that increased yield could be secured in flat measures by flushing the openings (breasts, etc.) with sand, crushed rock, etc., as referred to in Bulletin No. 25 before mentioned, in beds of almost any thickness; but in steep pitching measures there is some doubt of the applicability of this system in beds exceeding 15 to 20 feet thick, or in free-running seams.

From the figures shown in a preceding chapter it will be quite evident that the supply of Anthracite coal is by no means "unlimited," and that the conservation of the remaining mineral should be the earnest study of everybody having anything whatever to do with the production, marketing and consumption of this invaluable natural product.

While the Mining Engineers have much to learn, and room for improvement, in the way of conservation, we believe the Mechanical Engineer is as greatly interested in conserving the heat units of the fuel delivered to him, and that there is in this department, considerable room for improvement.

In conclusion we desire to call the reader's attention to a fact, —which is prominently set forth in the foregoing and is abundantly proved by the history and experience in the Anthracite Coal fields of Pennsylvania,—an economic law of universal application to all sorts of natural resources, which must be faced by all conservationists everywhere, namely; that short tenure of title leads to small operating units, careless methods and extravagant waste of the natural resources, while long tenure promotes large operating units and scientific methods, resulting in the greatest possible conservation.

The deeper and more expensive mining of the present day leads, of course, to greater cost, and scientific methods with a resultant conservation would also add to this, and consequently increase prices to consumers; but with the increased prices greater conservation may be secured. How much of this burden the present generation should bear for the benefit of the future is entirely a commercial problem.

PROGRESS IN DEVELOPING AND CONSERVING WATER SUPPLY FOR MUNICIPAL AND DOMESTIC PURPOSES

ALLEN HAZEN
New York, N. Y.

The progress in developing public water supplies in the United States may be stated in a broad way to have consisted in developing and securing such supplies as have been required up to the present time. In general, development somewhat precedes requirement, and in some cases, sufficient water is now available to supply the needs after ten, twenty, or even thirty years of probable growth. In other cases, the supplies now available are only adequate in years that are not especially dry, and would be inadequate under conditions of continued dry weather which recur from time to time.

In many parts of the United States, water is available for all required public water supplies, without special effort being made for its collection and conservation. This is especially true of cities located on rivers of considerable size and upon the Great Lakes. In these cases it has often proved necessary to prepare the water for use by purifying it; but from the broad standpoint of securing water, no serious difficulty has been presented.

In other parts of the country, water is obtained for supply from relatively small streams by building reservoirs in which flood flows are stored and made available for use in dry periods. Many of the largest cities in the country, including New York, Boston, Baltimore, San Francisco and Denver are supplied in this manner. This general method is especially used in hilly country, and often has the advantage that the water may be supplied by gravity, thereby saving the cost of pumping. This advantage is so considerable that storage reservoirs are often used even where rivers are at hand which would furnish a sufficient quantity of water. There are also certain sanitary advantages growing out of the use of stored upland water, which have frequently been of importance in determining the selection of these sources.

Water Supply Possibilities in the United States

The water supply resources of this country are very great indeed. No one knows, or can know exactly how great they are. They differ with climate and topography. They are relatively less in the arid and sub-arid regions of the west and on the Southern Pacific coast. In this great area, the whole available water supply will be developed and used, either for water supply or for irrigation, at a date that in the history of the country is not remote. Through the middle states there are occasionally cities located near the head waters of streams where there is, or will be difficulty in securing water in large quantities without transporting it for longer distances than have been considered feasible up to the present time. With these exceptions the water resources of the country are so great in comparison with the requirements of domestic use, that they may be considered practically unlimited.

Their aggregate amount is not known because no limits can be set upon the amount of water that may be obtained ultimately from the various areas. It would take most extended and detailed studies of these areas to determine their possibilities. Such studies have been made for a few limited areas now used for water supply, as for instance, the Croton River now supplying the City of New York, and Esopus Creek, to be soon added to the supply. The great majority of streams have never been adequately studied to determine the possibilities of storage upon them, and there is no reason why the expense of such studies should be now incurred.

The results would be only moderately conclusive, even if they were made in the most thorough manner now possible. Methods of purifying waters that have been developed in the last ten years have made fundamental changes in ideas as to the availability of many sources, and have added greatly to the field. In a similar way progress in the whole art of water works construction, including pipes, conduits, tunnels, pumps, dams and reservoirs, has steadily increased the field from which water may be successfully drawn. Increase in population also increases this area, for the cost of carrying water long distances decreases relatively as the quantity to be carried is larger. A city of a million inhabitants may go a hundred miles for water with no greater relative effort than is represented by a few miles of pipe laid by a country village. On the other hand the development of the resources of the country involves the use of water and land for other purposes, so that each year many excellent sources cease to be available.

In a strip of land 400 miles long and 50 miles wide, extending from Boston to Washington, are located many of the largest cities of the United States. In this region more water has been developed for public water supplies than in any other corresponding area in the world. The amount is larger than in densely populated European areas because our per capita consumptions are several times higher; but with this done, the water resources available to this region have not been exhausted. It is true that in the immediate neighborhood of Boston and New York the most available supplies have been developed and utilized, and it is necessary to go somewhat further for additional water; but if there were demand for more water and a market to sell it at remunerative prices, physical resources are available so that an enormously greater quantity could be supplied. Without attempting a close estimate, it may be said that at least ten times the amount now supplied could be furnished, and probably a much greater quantity. This would mean the storage of at least a part of the flood waters of some of the larger rivers, such as the Connecticut, the Housatonic, the Hudson, the Delaware and the Susquehanna, thereby utilizing sources enormously greater than any now used, and which, as yet, have not been touched. To carry out such works would involve great dams, reservoirs and tunnels, and aqueducts larger but not longer than some that have been already undertaken. Railroads and towns would have to be moved, and the whole work would be carried out on a scale not justified by the present demands for water.

That which applies to this small area of greatest density of population, applies in even greater measure to most of that part of the United States east of the arid region.

Conflict of Interest between Cities

It frequently happens that a source of water supply that is selected by one city is also physically well adapted to use by another. Each city desires to secure the control of that source or sources which can be most economically and advantageously used for its own purposes, and many conflicts have grown out of this condition. Until recently the city or company or individual that was first upon the ground and acquired sufficient property to control the situation, or secured the legislative authority to take the same by the exercise of eminent domain, held it to the exclusion of all others. In recent years a number of states where cities are near each other, have established methods by which rights in new sources of supply could be acquired only after procedure intended to prevent cities, corporations or individuals from acquiring more than their fair share of water, and to protect the assumed natural right of each municipality to have for its own use the source or sources of supply most convenient and natural to it, as far as the same is not inconsistent with the like rights of its neighbors, and in case of conflict, to make as fair a division as possible.

Conflicts of this kind have given rise to much discussion and have created an erroneous impression of scarcity of water. As a matter of fact such conflicts do not necessarily or ordinarily indicate a scarcity of water. They indicate the desire of two or more parties for control of a source more cheaply developed or otherwise more advantageous than others, or supposed to be so.

Community of Interest in Water Supply

Another problem similar to the last, but differing in its manifestation, is presented, where two or more cities are so situated that they can be more economically served by natural resources by one system of works than by independent systems. Cases of this kind are numerous in the older and more densely populated parts of the country, where it is frequently necessary to transport water for much greater distances than the average distances between adjoining municipalities.

The cost of transportation is often an important part of the whole cost of the water, and this cost is reduced by using one or two large lines, as compared with several smaller ones.

To secure this and other economies of combined action, water districts have been formed comprising several, or a considerable number of municipalities. In other cases water companies have supplied groups of communities. In some cases the whole water business has been consolidated under one management. In other cases the management of the distribution systems has remained local, and water has been supplied at wholesale to the local works which have preserved their independence by acting as retailers only.

Property Available for Water Supply also Available for Other Uses

In most cases water suitable for a water supply, and land suitable for developing it, are also available for other uses. As the water resources are enormously greater than the needs of domestic supply, it naturally follows that most of the water and most of the property, from a physical standpoint, available for developing it, are not in actual use for furnishing water supply, and generally the water and the properties are taken up and used for other purposes. This is not only a natural result, but it is the best arrangement considered from the standpoint of the development of the whole country. If all the water and all the land that might possibly be sometime used for water supply were reserved from other uses, it would result in an unwarrantable tying up of the resources of the country, and would work great injustice.

Some of the uses to which such water and property may be put are not incompatible with their use for public water supply. Without attempting a complete statement, a few examples of such double use may be given. As a first example, public parks upon the gathering ground of a water supply system are not objectionable and where large parks are desired and areas are also to be reserved for water supply purposes, it is in the interests of conservation of the resources of the country to use the same areas for both purposes as far as possible.

As a second example: in mountainous districts it frequently happens that economical sites for storage are high in elevation and would furnish more pressure than is desirable, from the standpoint of economical transportation and use of the water. In such cases some of the elevation may be used for developing power. The development of a source in this way for one purpose does not interfere, but rather aids the other, and a joint use for power and water supply is advantageous.

As a third example: the presence of farms and ordinary rural communities upon the catchment areas of water supplies is not usually or necessarily injurious to the water to such an extent as to justify the elimination of such occupation. The methods of treating water and of protecting it against the possible results of pollution have so advanced in recent years, that there is even less reason than formerly for wishing the elimination of population. A great majority of the water supplies of the cities of the world are drawn from areas containing considerable populations, and this condition is to be recognized as one likely to continue. It is true that some kinds of occupation are more unfavorable than others to the quality of the water, and it is proper and desirable that authorities managing water supplies should have some voice in the management of the area from which water is drawn, and some power of discouraging those uses which tend to impair the quality of the water. But with such reasonable control as experience shows can be readily exercised, good water may be obtained; and the greatest use of the resources of the country will be obtained by permitting the land to be used and occupied for such reasonable purposes as it is best fitted for.

Occupations of Land not Compatible with Water Supply Development

If one follows up representative rivers in a hilly country, especially the smaller rivers in New England, or other densely populated portions of the east, a succession of dam and reservoir sites is frequently presented, which, from a physical standpoint, might be utilized for storing and making available the flood flows of the streams. These reservoir sites are commonly the most productive and valuable lands; and they frequently afford the best sites for towns and cities. Hundreds of New England towns are located on ground which, under other conditions, might have been the floors of reservoirs; and the sites for the high dams that might have formed such reservoirs are occupied by mill dams of only moderate height. Railroads frequently follow the streams. To utilize such possible sources involves buying all property, removing the villages, buying out the mills and moving the railroads above the flow lines of the proposed reservoirs.

When a great city is looking for a water supply to serve the added needs of the growth of a generation, it can afford to buy out villages that are not too large and to re-locate railroads, and to do the other things that may be necessary to utilize a supply in such a location. This is a matter of degree. There are limits beyond which even the largest and richest cities may not go. Some of the best reservoir sites are occupied by thriving towns and cities, and are seats of industry to such an extent that they can never be used for water supply purposes. Other natural sites are remote from development and the lines of progress, and can be secured. It is often a question of buying out and utilizing a naturally economical but now otherwise occupied site near at hand, or carrying the water from a more remote site which can be obtained, with less disturbance to existing conditions.

Water Power Developments

In the last ten years there has been a great increase in the use of streams for water power. Before that time water powers were mainly obtained by the utilization of the permanent or nearly permanent flows of the larger rivers where there were natural falls. Progress in the art of developing and utilizing water power, and of carrying it by electricity from places where it is obtainable, to places where it can be used advantageously, has resulted in construction of reservoirs upon the upper waters of many smaller streams where the stored waters can be utilized through a considerable fall to generate power at all seasons of the year.

The development of such powers has thus begun. In the next generation the number of such works will be increased many fold. This represents a conservation of natural resources which adds to the wealth of the country, and is desirable in every way.

The streams utilized in this way are, however, streams that would otherwise be physically available for domestic water supply, so far as there is, or may sometime be demand for the water.

To some extent these uses are not incompatible with each other, especially in mountainous country, when the differences in elevation are great, but broadly speaking there is a considerable conflict. If a stream is used for water supply it is not available, or not as readily available for water power, and if it is used for water power, it often ceases to be available for water supply. There are many cases where more remote and less desirable supplies have been selected because nearer and more available sources have been previously developed for power. As the number of such sources is generally much greater than the number that would be required for water supply within any period of time that may be legitimately taken into consideration, no general effort to limit the utilization of these sources for water power is to be desired.

An ideal arrangement would be for each city to look well ahead and see what it will need during a reasonably long period, and to secure the rights and such land as may be necessary for its development to control such supply. When this is done if the source can be used for power in the interval before it is required for water supply, and if the conditions are such that a water power would pay during such period, arrangements might be made by lease or otherwise for the development of the power, subject to the right of the city to take it for water supply when occasion demanded. The works for storage might appropriately be the same for water power as for water supply, and the same tunnels and some other main parts of the works might also serve, so that a substantial part of the investment for power would serve afterward for water supply.

Under such an arrangement, when it became necessary to take some water for domestic purposes, there would still be water available for power. During a long period of years the amount of water for domestic supply would gradually increase, while the amount of power would gradually decrease.

American cities do not have the powers necessary to carry out such a comprehensive plan, and the arrangement suggested is, therefore, an ideal one, which might be brought about under a more perfect form of Government than we have yet reached. It would be in the interests of true conservation of natural resources to make such an arrangement possible.

Irrigation

In the arid west the law of water is different than the law of water in the east. This is natural because in the arid west water is the most valuable element. Water is the source of life; and the development that can be reached in any locality is directly dependent upon the amount of water that can be permanently and reliably furnished. The laws of the western states are the outgrowth of experience in these climates, and have resulted from efforts to distribute the water as equitably as possible among those who have the best right to it and make the best use of it.

In the east it is common for a city to acquire, through the aid of the state, the exclusive right to all the water to be had in a certain source. This rarely, if ever, happens in the arid west. Appropriations of water are made and these appropriations are served in the order of their priority. That is to say, the man who first locates upon a stream and appropriates water for his use has the first right to use it ever after.

There is uncertainty at the start as to how much water will be available, and great uncertainty among the appropriators as to how much they will be able to use, and each is left to appropriate that which he sees fit. All the waters of the streams in the arid region have been appropriated many times over. For an appropriation to be valid, the water must be actually used and in general, appropriation is only good for so much water as is actually available and put to beneficial use.

Carried to its logical conclusion, this may mean that the city can only really hold rights to the water which it now uses, and that all rights for more water than it now uses are somewhat uncertain and liable to be replaced by junior appropriations. The laws tend to make it impossible to hold water that is not used. If a man owns water and does not use it, the man who came after him with a junior appropriation and does use it, soon acquires the right to use it, and the first appropriation ceases to have value. This may be good policy as between individuals, but it puts a growing city in a very hard position, because the use of water is constantly increasing, and it is only reasonable that water for a moderate period in the future should be controlled and held in reserve. Practically this has been done and is done in some cases by various methods suggested by the ingenuity of those having to deal with these problems.

There is also a question as to whether a city having acquired certain rights for domestic water supply may legally use them for other purposes before they are required for the use for which they were acquired.

With rapidly increasing values of water in the arid region, there is great need of having the whole matter determined by a simple adequate law, so that a city may firmly hold such rights as it needs and is able to acquire, and it is desirable, from the standpoint of the greatest use of resources, that the rights so held may be put to other uses in the interval without prejudice to the permanent right to use them for water supply. Amendments to the constitutions of some of the states may be necessary to clear up these matters.

The Right of Eminent Domain

It is commonly recognized that the use of property for water supply purposes is more important to the public than the use of water for power or irrigation, and legal methods are provided by which properties required for water supply may be taken, and compensation made to those who are injuriously affected by the new use. The exercise of such powers is common and is well understood. The courts always protect carefully the rights of those who have occupied and owned the property. The only justification for taking it for water supply purposes is that it is more valuable for those purposes, and sufficiently so, to justify the taking. The forced sale is often something of a hardship to property owners, even though full value is given.

The consideration of these two main fundamental propositions commonly leads to the payment to the property owners of sums of money in excess of the fair value of their land or rights for any other purposes but those of water supply. This must be accepted as an inevitable condition, and those who think that cities ought to be able to buy up farms for reservoirs at prices no greater than the land could be sold for for farming purposes, will be disappointed in the awards that are made by the courts. On the other hand the excessive awards for land that have sometimes been made are unfortunate, and tend to discourage carrying out projects that are in the public interest. Generally with good administration it has been possible to acquire properties at an advance over their values for other purposes that is not unreasonably great, when taken in connection with the increased value of the property for water supply purposes, which is the only justification for taking it.

Anticipating the Future

One of the most interesting and difficult questions presented is as to how far a city really ought to anticipate the future in acquiring land and rights. If it were said, our city has 100,000 inhabitants, and in a century will have a million, and we shall then require so many gallons of water per capita, and it will take such and such areas to supply this water, and we propose to buy them now, the result might easily be burdening the present generation unduly with interest charges on bonds issued to pay for remote and even speculative requirements, for it is quite possible that the increase in population may not be as great as assumed, and it is equally possible and probable that the habits of the people who live in another century will be different from ours. It may be that more will be required or it may be that less will suffice. It is only necessary to mention the shower bath and the swimming pool to suggest the great uncertainty of the remote future.

Then there is the certainty that there will be great developments in the whole business of water supply, and the possibility that sources will be opened up not now considered available. If there were a magnificent source of supply near at hand which could be obtained at small expense, prudence would dictate the advisability of securing it. This condition may still exist in a few cases. Far more commonly to secure a liberal supply for a century would involve the expenditure of great sums of money to procure land and rights which would not be justified by the reasonable prospects of the case, and which ought not to be lightly undertaken. What then will happen? The properties controlling the sources will fall into other hands, and be put to such uses as they are fit. Water power is developed, the land is cultivated, railroads are built and the property becomes valuable. Many sources of supply otherwise excellent are used for other purposes to the point which forever effectively prevents their use for water supply. Towns and even cities are located in valleys which would otherwise form ideal reservoir sites. They cannot be moved with increasing demand for water. Instead other and more remote sources of water supply must be found and developed and the saving in land and rights may more than compensate for the added length of conduit.

If the water resources of our country were more limited, so that, for instance, all the water that could be produced was likely to be required for domestic and municipal purposes within a limited length of time, then it would seem desirable and necessary to study the water resources more thoroughly and to make outline projects for future requirements, and to make a greater effort to reserve the properties for water supply purposes. With conditions as they are, it may be questioned if this is feasible except in a few exceptional cases.

State Lines in Water Supply

The business of procuring, storing, distributing and selling water is under state control. That is to say, it is done by municipal and other corporations having state charters, and subject to state laws. The business is not regulated or controlled by the general Government. There are cases, including one very notable one, where the most economical and advantageous supply for a city is in another state; but one state does not have authority to build water works in another state, nor to authorize its municipalities to do so. There are instances of private corporations that have secured water in one state and sold it in another, but in many important cases the state line has been regarded as an insurmountable barrier. For this reason a supply partly on either side of a state line is usually considered not to be available for municipal use at the present time.

This is a matter where the Constitution of the United States at present seems to be somewhat inadequate to meet the present requirements. There is no logical reason why any city in this country should not have the privilege and all the rights that are necessary to develop a water supply wherever in its neighborhood it can be most economically and advantageously done. If existing laws do not permit this, as they apparently do not, the sooner this matter can be corrected the better it will be.

The Constitution of the United States prohibits the States from imposing duties on exports. It does not seem to prevent a state from prohibiting the export of a commodity. One state has done this with water, and has amended its constitution to this end. Probably the idea of this change in the law was that ultimately all the water resources of the state would be required by its own citizens, and that it was wise to prevent the diversion of any of the water into another state.

But from another standpoint, the action seems both shortsighted and unwise. If Pennsylvania were to say that all her coal would sometime be required by her own citizens, and that none of it were to be sent out of the state, it would be unfortunate for all her neighbors, but there would be some reason for it, because for each ton of coal sent out of the state there is one less ton left in the mines.

But with water, the case is different. The supply is renewed each year by the rains falling upon the whole surface of the ground and all unused water runs to the sea. If water supplies are developed and used, and all the water drawn from them that can be drawn during this century, there will be just as much water available in the centuries that follow as if not a drop had been utilized in this. If, instead of prohibiting the sale of water outside the state, provision were made for controlling it, or so that the rights would revert after a long period, water could be sold and profits realized on its sale through a period of years, which might be very long, and still there would be absolutely no reduction in the amount of water ultimately available to the citizens of the state.

On the other hand, developing supplies for use outside the state would tend to insure retaining the properties on which they rest for water supply purposes, while if they are not so used, some of them are certain to be used for other purposes, and will cease to be available for water supply before the time when they might be required for use in the state in which they are situated, and so far as this is the case, the prohibition of present use means permanent loss of these sources of water supply.

Compensation in Kind

The American laws and courts require compensation for water that is taken by eminent domain in money. The compensation is calculated upon the theory that when the right to divert water is obtained, the diversion of the water begins at once and is complete. In order to secure a valid right for the diversion of water from a particular source, it is customary and apparently necessary in most cases to secure the full right to the whole source. This practically results in the recovery by the riparian owners of damages for the diversion of all the water, and as only a fraction of the water is needed at first, the balance flows down the stream as before, and the owners continue to enjoy a large part of that which they have been paid for. Of course, conditions vary greatly. There are cases where diversion is comparatively complete from the start, but they are exceptions.

It frequently happens that the area from which water is to be taken is large and that flood flows from it are very great, and flow to the sea without advantage to anyone. In fact these flood flows are frequently destructive and do positive harm instead of good on their way. Taking a source for water supply frequently means building a large impounding reservoir and holding back these flood flows to fill the reservoir. It is sometimes possible to so manage the business that only flood flows will be taken for water supply, and that the moderate flows of the stream will remain undiminished. In England this procedure has been established by law and is called compensation in kind. That is to say, the law provides that when a stream is taken for water supply, the storage provided shall be sufficient to not only furnish the water taken for domestic supply, but also to maintain flows of the stream which are regulated by procedure so that riparian rights below will be no less valuable than they were before.

In a number of cases arrangements of this kind have been carried out in America voluntarily. Such arrangement may be mutually advantageous because it relieves the water undertaking of heavy water damages and at the same time, if properly carried out, insures the power owners against loss of power, and in fact practically may even give them more power than they had before. Legal recognition is needed to enable this most useful procedure to be carried out fully, and with the best results.

CONSERVATION AND USE OF WATERS IN THE RECLAMATION OF ARID LANDS THROUGH GOVERNMENTAL AGENCIES

F. H. Newell

U. S. Reclamation Service, Washington, D. C.

Under the terms of the so-called Newlands Act of June 17, 1902, the United States has invested upwards of $70,000,000 in the building of reservoirs for the storage of flood waters and in canals and related structures for taking these and other available waters to lands which in their natural condition have such a small supply of moisture that valuable crops cannot be obtained each year.

The moneys for this purpose are obtained from the disposal of portions of the public domain, and as the lands are disposed of the moneys received are put into a fund in the Treasury. These moneys are then expendable under the direction of the Secretary of the Interior in his construction of the works above mentioned. When these works are completed to a point where water can be brought to the lands, these latter, if in public ownership, are opened under the terms of the Homestead Act in tracts of not more than 160 acres in extent, the size being limited by the area which in the opinion of the Secretary of the Interior will be sufficient for the support of a family. This averages about 40 acres. In some cases it is as small as 10 acres.

The public lands thus reclaimed are given away on condition that they are cultivated and actual residence established and maintained during five years. The estimated cost of bringing the water to the land, including the construction of the reservoirs and all administrative and relative charges, must be repaid by the homesteaders or by those purchasing private lands to which the water may be brought. The payment is made in annual instalments not exceeding ten; for example, if the cost of storing and bringing the water to the land has averaged $30 per acre, the homestead entryman or purchaser of the land is required to pay $3 per acre per annum for ten years. The amount thus received goes immediately into the Reclamation Fund and can be expended at once without further act of appropriation. Thus the Reclamation Fund is what has been termed a revolving one, being continually returned. At the same time it is being increased in amount by the additions from the disposal of other lands not taken up under the terms of the Homestead Act.

The works are widely distributed and have been built in each of the western states, from the Rocky Mountain region to the Pacific Coast. These states in alphabetic order, are: Arizona, California, Colorado, Idaho, Kansas, Montana, Nebraska, Nevada, New Mexico, North Dakota, Oregon, South Dakota Utah, Washington, and Wyoming. The irrigated land will extend into the state of Texas from works built into New Mexico and experimental construction has been undertaken in Oklahoma.

The works already completed or nearing completion furnish water for a little over one million acres and when finished the projects now in hand will supply nearly three times this area. The number of farms irrigated is, in round numbers, 14,000. There are now being operated nearly 5,000 miles of canal and the value of crops obtained from lands thus being served with water was over $13,000,000 in 1911. It is estimated that a population of very nearly 70,000 persons, exclusive of those in the cities and towns, is now dependent upon these works.

The act of Congress as originally passed was very broad in its provisions, and simply indicated the results to be attained. In the ten years which have elapsed since the passage of this act, a vast amount of executive detail has been developed, additional legislation upon minor matters added, and an organization built up competent to handle the widely scattered work. The wisdom of the act has been demonstrated by the success attained and the optimistic predictions of the framers of the act have been amply verified.

The work in many respects has been pioneer in character. The country in which the projects are constructed is sparsely settled, the structures themselves frequently remote from railways or other lines of communication, and it has been necessary for the employees of the Government to enter into many details which appear at first sight to be quite foreign to the object of the law. Thus it results that the operations being distant from the railways in some cases, it has been necessary to build these and as it was impossible to deny to the scanty population the conveniences of these railroads, it has been necessary to operate them upon a commercial basis.

One of the principal items for construction is Portland cement. In the case of the Roosevelt dam in Arizona, this was so far away from railroads, and conditions were such that it was found desirable for the Government to build and operate its own cement plant. Incidental to much of its work it has been necessary to operate commissaries, boarding houses, mercantile stores, hospitals, and enter into an infinite variety of matters which would not be necessary in an older country. It has been necessary to bring together hundreds of workmen and subsist them and their families in remote places, and thus has resulted the development of many enterprises carried on by the Government, which would not be necessary excepting under pioneer conditions.

From the standpoint of the chemical engineer, the most interesting of these operations are possibly those which relate to the development of water power in connection with the conservation of waters for use on the dry land and the employment of this power coincident with its use in irrigation. The storage of flood waters in the mountain valleys makes it practicable to control the flow of certain streams through a great part of the year, and the water in passing from the point of storage to that of use descends in many localities at such rapid rate as to furnish facilities for water power development.

In earlier decades water powers were used to a considerable extent at factories distributed throughout the mountain country. Later the inconvenience of going to the water power resulted in steam largely displacing it as the most important agency in manufactory. Then came the development of electrical transmission by which the water power could be brought to centers of population, and again water power came into prominence in industrial affairs. But one of the conditions of success with hydro-electric power is that of continuity of service day by day without intermission throughout the year. In the case of water stored for use in irrigation, the maximum demand comes during the hot period of summer or during winter. In the season when crops are not growing the water is not needed and should be stored. Thus we have an excess of water for power during the summer or crop season and little or no water available for power during the remaining months.

Under these conditions of summer supply only the water power obtained from works built for irrigation has relatively little value, especially in the ordinary uses of lighting, transportation, etc. But there have been found to be certain chemical industries where the time element is not very important. Thus it results that much of the water power which would otherwise be unavailable can be utilized for chemical manufacturing in connection with, but secondary to, the demands for irrigation.

One of the industries which it is hoped may be developed is that of the making of fertilizers by fixing the nitrogen of the air by means of the electric current developed from the waters stored for irrigation and released during the crop season. In all irrigated countries there is a great need for fertilizers. There is a popular fallacy that irrigation water brings all that is needed for the growing plant, but this is not true. Under intensive cultivation such as is possible by irrigation, there is great need for fertilizers. Very few, if any, of the natural waters, even though carrying considerable sediment, supply the nitrogenous matter needed by the crops.

In a less direct manner the operations of the Reclamation Act have interest to the manufacturing chemists of the country, in that through the conservation and use of the waste waters employed in the cultivation of the waste ground, there is developed a market or necessity for all of the articles which enter into the operations of daily life. The putting into the waste places of the country of a dense population of prosperous farmers results in a demand for manufactured products (including those from various applications of chemistry) to a degree unequaled by any other form of development. The soil when properly cultivated in the arid regions, where the sunshine occurs daily throughout the year, has a degree of productivity unknown elsewhere. Where intelligently handled the small farms yield a return which enables the owners to enjoy more than the average share of profit, and hence these farmers are not only producers of raw material, but the best and most reliable consumers of manufactured articles of any class of people.

When it is comprehended that the owners of these small farms would probably have been unable to secure homes in any other way and that the individuals are taken largely from the non-productive class and converted into producers of wealth from the soil, it will be appreciated that the action of the national Government in utilizing its resources in this manner is not only wise in adding to the prosperity, but to a certain degree is one of the best insurances of the continuity of national life. The owner of the small intensively cultivated farm is one of the most progressive of citizens and at the same time conservative so far as those things which affect the stability of the Government and of its institutions.

The operations under the terms of the Reclamation or Newlands Act are committed to the Secretary of the Interior. He has authorized the creation of an organization or bureau known as the Reclamation Service, at the head of which is a Director, reporting to the Secretary and responsible to him for the planning, initiation and conduct of details as authorized by the Secretary, The principal executive officer under the Director is a Chief Engineer, who in turn has 6 supervising engineers located at convenient points in the west, each supervising engineer being the local representative of the organization. The Director and Chief Engineer alternate in the Washington office and in the field, dividing or sharing the duties of the field and office work, the Director giving principal attention to the larger administrative matters and the Chief Engineer to the more purely technical details.

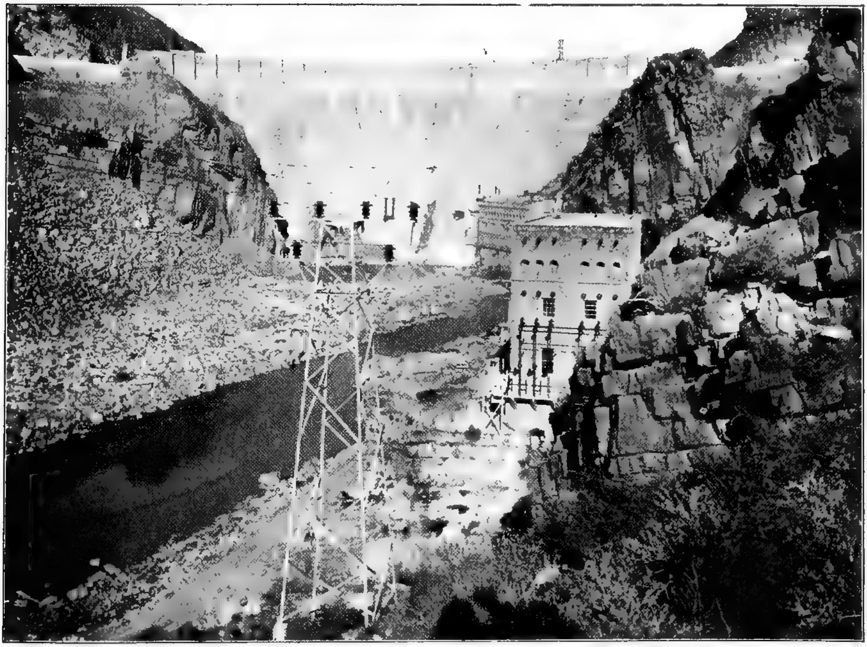
Each supervising engineer has charge of a number of projects located usually in different states. These projects cover considerable areas, being sometimes from 50 to 100 miles in length, and the project engineer or manager must spend his time largely in moving about over the project. Each separate feature is under the direction of a resident engineer or superintendent, who reports to the project manager. For example, during construction the project engineer has general charge, and if a large storage dam is being built perhaps 50 or 100 miles away, there is a resident engineer on the ground in immediate charge and another engaged in the building of the diversion dam, distributing canals, etc.

Each of these resident or constructing engineers and superintendents of construction has one or more engineering and technical assistants and each project is provided with a chief clerk, who supervises the bookkeeping, costkeeping and all the details of records and correspondence.

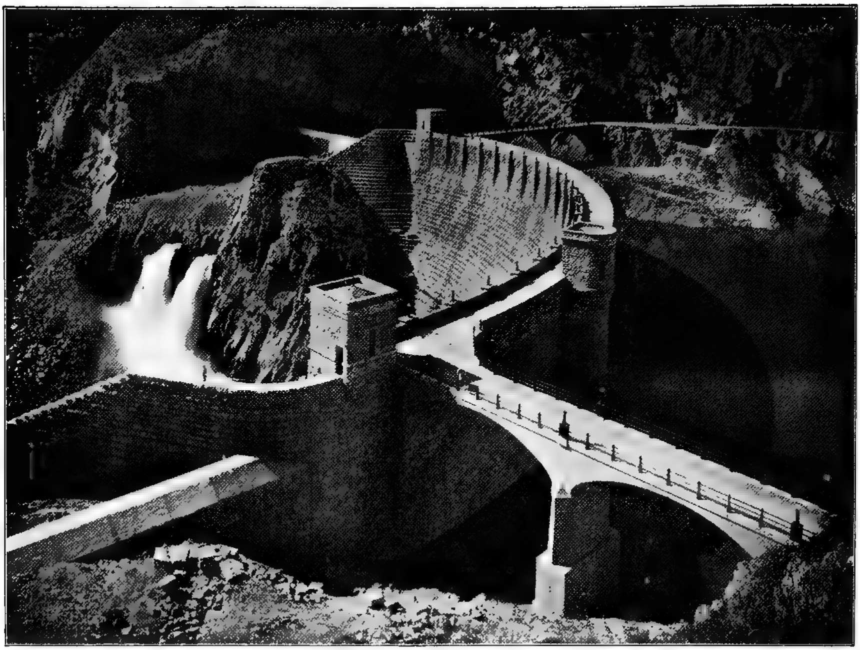
The Reclamation Service as a whole embraces about 1,500 persons appointed after competitive Civil Service examination, and employs from 5,000 to 7,000 laborers, the number varying from day to day according to the work in hand. Much of the work is done by contract, especially by a series of small contracts in which the work is divided up into items of such size and character as to be readily described and bid upon by experienced men. That is to say, instead of attempting to let a large amount of work in a single contract and to throw upon a single contractor the responsibility of many ramifying details, it has been found far more economical to subdivide the work, the Reclamation Service occupying the position itself of the principal contractor and apportioning the operations to what would otherwise be subcontractors. For example, in building distributing systems involving many miles of canal, these are subdivided into portions of a mile or two and over in length, so that the farmers may bid upon as much or little as desired and may thus earn the money needed to establish themselves on the land and pay to the Government the cost of water delivered to their farms.

In the construction of tunnels for conveying water and in the building of dams where the foundations are far beneath the surface, it has been found more economical and effective to do the work by Government forces than to endeavor to let it by contract. The risks involved are so great that the contractor must either bid in such a way as to afford him a large margin to cover contingencies, or if he bids too close and his bid is accepted,

Pl. IA. Cement mill in foreground, contractor's camp in rear near Roosevelt dam site, Arizona.

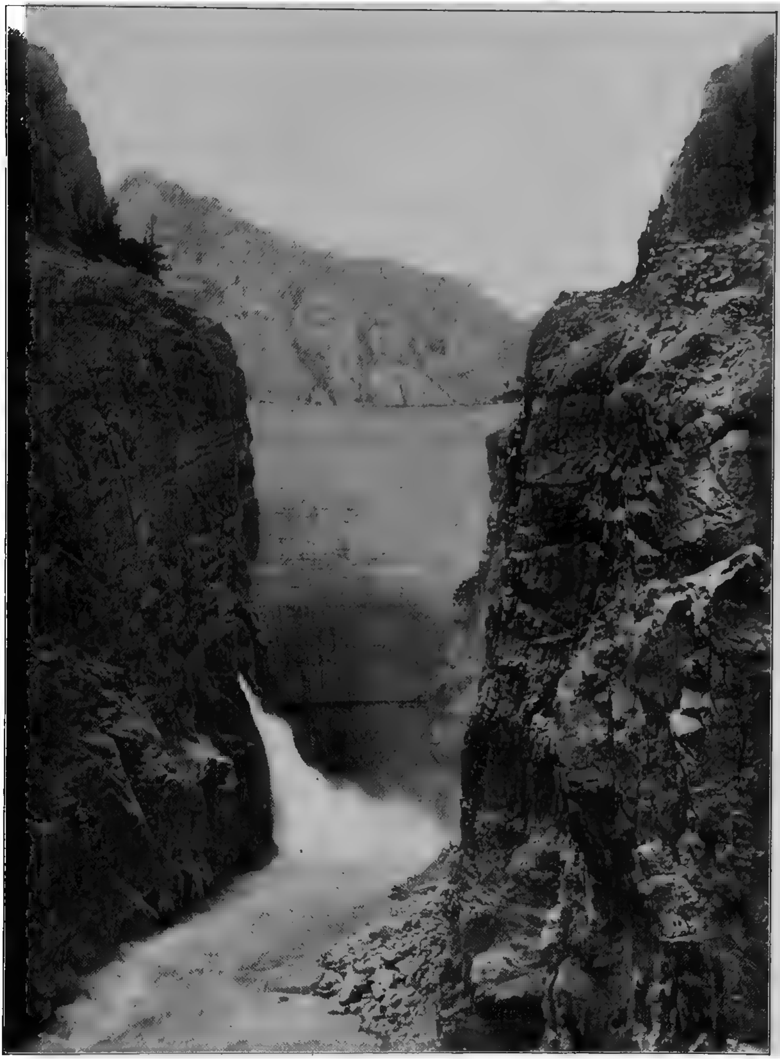


Pl. IB. Power plant utilizing stored water for generation of power at times when it is turned out of the reservoir for irrigation purposes.

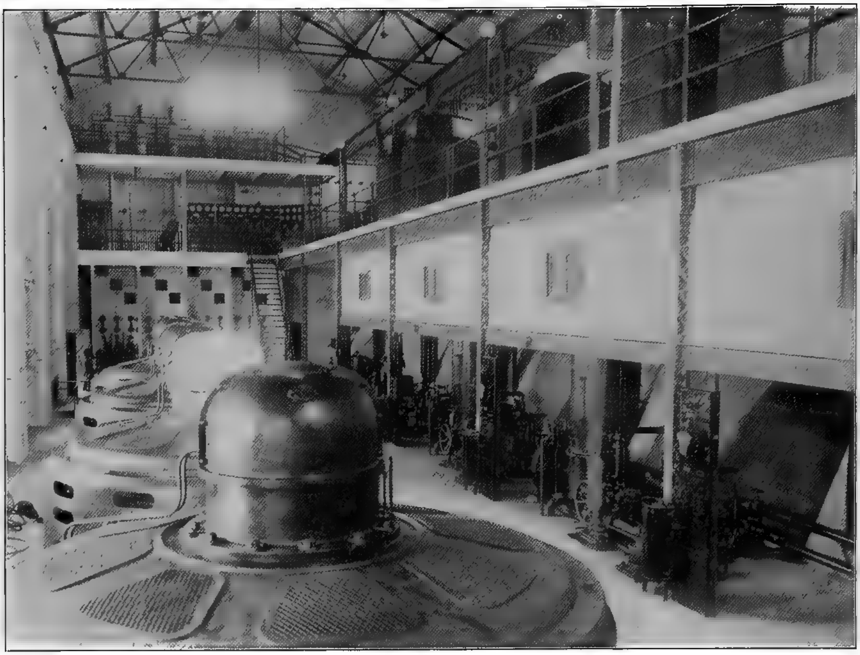


Pl. IIA. Roosevelt dam, Arizona, view from above showing stored flood waters.

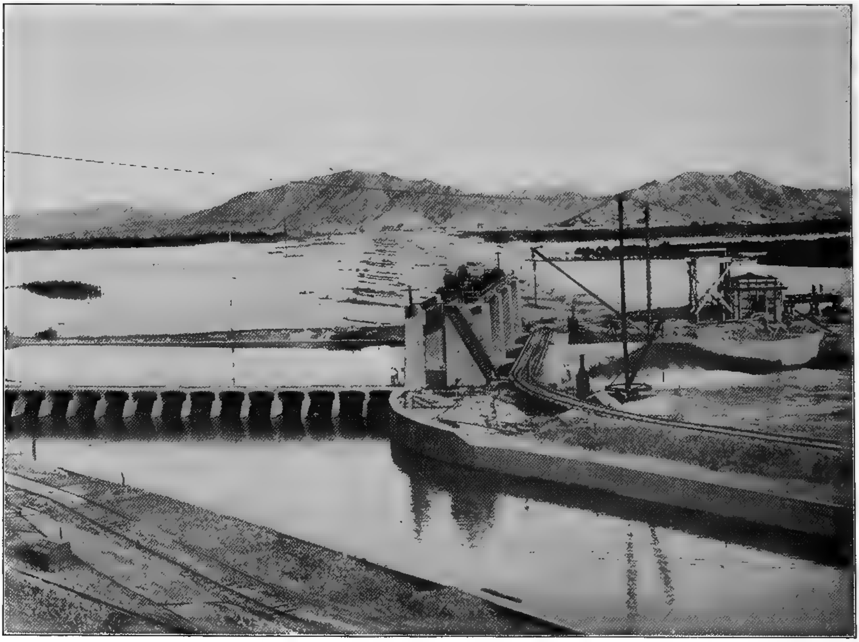
Pl. IIB. Jackson Lake dam at head of Snake River in Wyoming holding waste waters for use on desert lands in Southern Idaho.



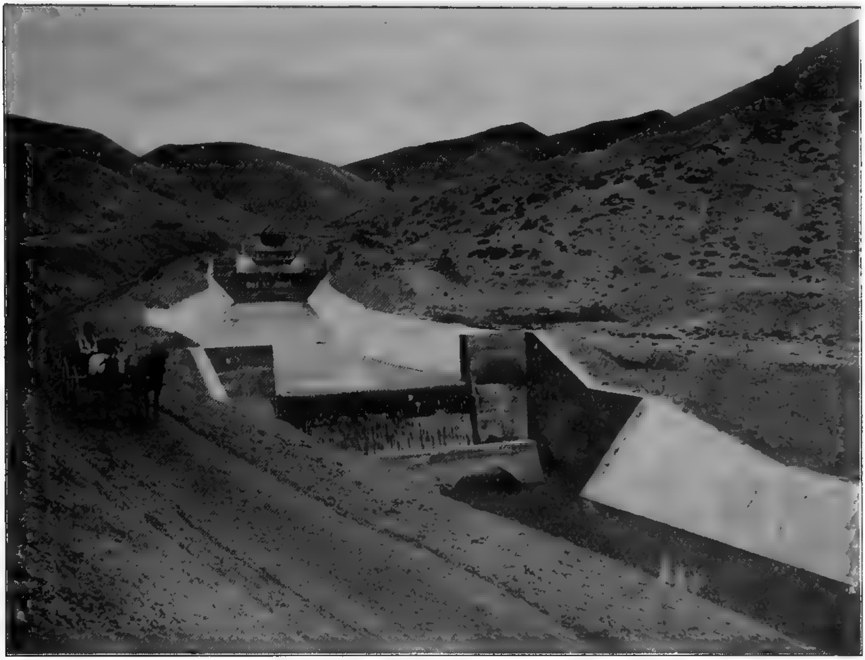
Pl. VIII. Shoshone dam, (highest in the world, 327 feet high) on Shoshone River east of Yellowstone Park, Wyo., for holding flood waters.



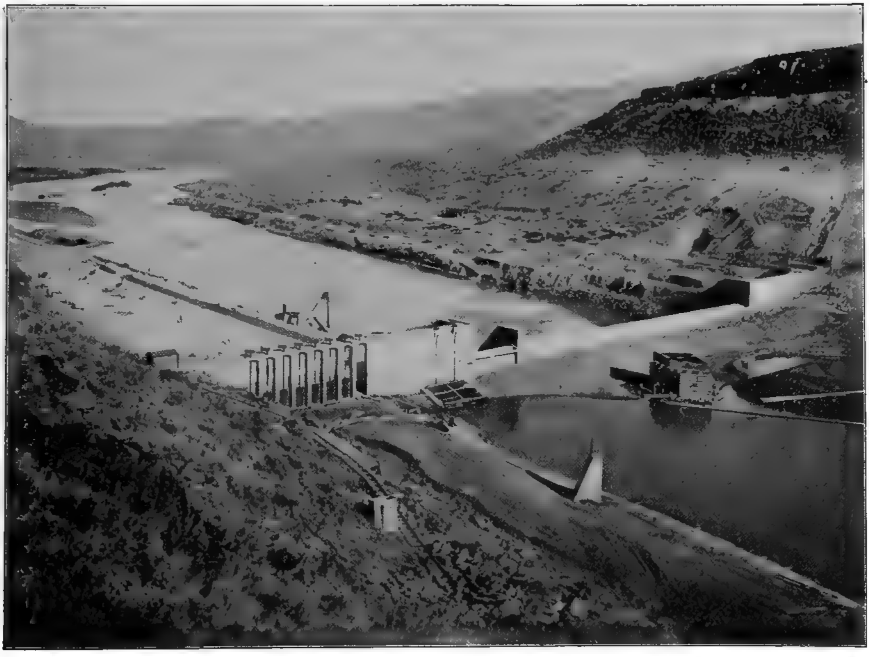
Pl. IIIA. Interior of power plant at Minidoka, Idaho, operated by waters controlled by irrigation works built for Minidoka project.



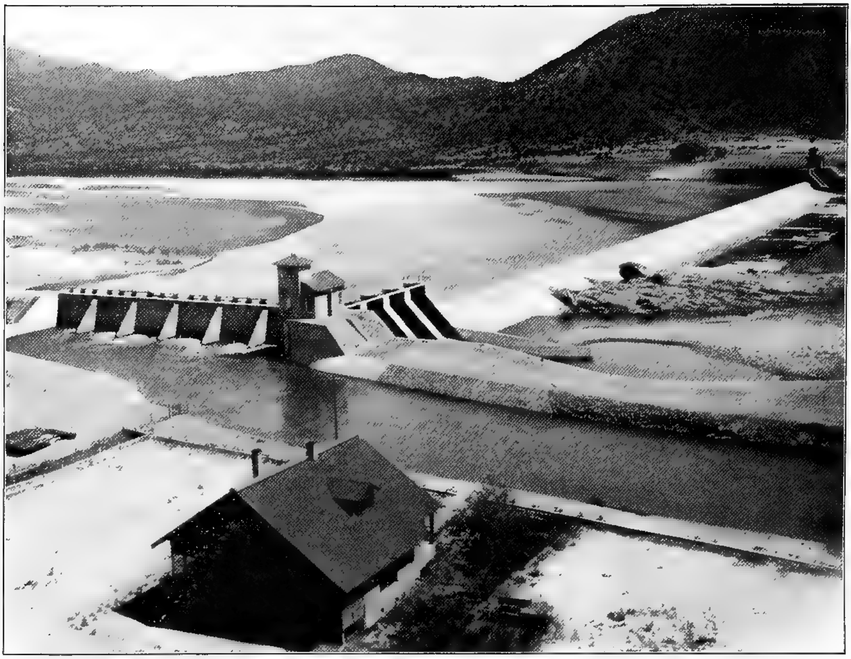
Pl. IIIB. Laguna dam on Colorado River looking from the California side easterly to the Arizona shore, dam is 4,000 feet long. In foreground is skimming device for taking out the less muddy waters.



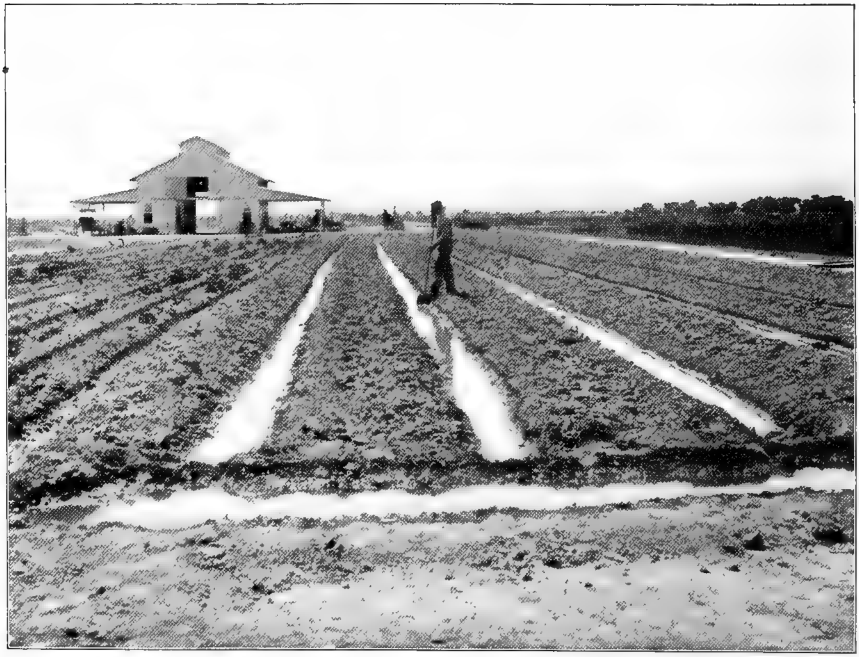
Pl. IVA. Drops on South Canal, Uncompahgre project, Colo., taking otherwise useless Gunnison River waters to Uncompahgre Valley; method of dropping these waters to the Valley.



Pl. IVB. Dam on Boise River to divert flood waters into the storage reservoir. View at time when large canal is being lined with concrete and low water flow of the river is being diverted through lower sluices.



Pl. VA. Diverting dam on Salt River, Ariz., showing in foreground the head of the northside canal and on opposite bank the corresponding heading of south canal.



Pl. VB. Methods of distributing irrigation water to the desert lands.

Pl. VIA. Distributing canal and structures on North Platte project, Nebraska.

Pl. VIB. Stack of alfalfa grown upon land otherwise worthless, excepting for the use of waters conserved and distributed by the Government system.

the losses usually force him into bankruptcy with corresponding delay to the work and increase of ultimate cost to the Government. The confusion and litigation which has resulted from the failing contractors on pioneer work of this kind more than overbalances any possible saving by letting such work by contract.

In the ten years which have elapsed since the passage of the Reclamation Act, the organization of the Reclamation Service has been developed, many notable structures built and large experience gained in operations of this character. The work has been conducted with a high degree of economy and continual efforts have been and are being made to improve in every possible detail. As a result of the character of construction initiated by the Reclamation Service all companies or associations entering upon reclamation by private capital have been induced or forced by public opinion to adopt similar methods of construction and to substitute instead of temporary works of wood the more permanent structures of concrete and iron. The development of the country has been greatly stimulated and altho the Reclamation Service has not reclaimed and will not irrigate more than a portion of the irrigable area, yet the results attained by it have greatly encouraged and stimulated private and corporate efforts and served as a standard for them.

It may be said that the larger problems of organization and construction have been solved, altho continual improvements are being made. The most difficult period of the work, however, is now being entered upon, namely that of operation and maintenance of the completed works and especially of the dealings with the thousands of farmers and collection from them of the cost of the work.

While construction is under way and money is being spent by the Government, there is little criticism but when the time arrives that these expenditures must be recovered in small payments from the farmers, then arises a critical attitude and an attempt to ascertain whether it is not possible to avoid repaying to "rich Uncle Sam" the investments made on behalf of the hard-working farmers! This is perfectly natural because the public has been educated by gifts of seeds and beautifully illustrated publications to the belief that the generosity of Uncle

Sam is unbounded and that there is no limit to the expenditures that he may make.

In the case of the reclamation fund, however, there is a very definite limit. Any concession granted to one man or set of men in the nature of delay in repaying the expenditure means the depriving of another man or set of men of a corresponding benefit. It is this condition which is depended upon to bring about a true appreciation of the opportunities afforded by the Reclamation Act and a safeguard of the Reclamation fund, namely the needs of the man who has not yet obtained adequate water supply may be depended upon to force the man who has already obtained water to make payment for the benefits received.

The cost of water provided by the works built by the Government may be said to range in general from $30 to $40 per acre. In some cases it has been as low as $22 per acre, and in others as high as $93 per acre. Without the water the land is practically valueless. With an assured supply the land when properly cultivated will pay a good return on an investment of from one hundred to several hundred dollars per acre. The addition of the water allows the owner of the land practically to capitalize the sunshine, and altho the soil may not be of the best, yet with sunshine and water at the right time extraordinary crops may be produced, especially in the warmer parts of the arid region. Even in the northerly latitudes the crop production of forage is large enough to repay an investment of upwards of $50 per acre in obtaining water.

From the figures above given it might be assumed, and has been, that operations of this kind would afford wonderful opportunities for investment of private capital. There are, however, certain conditions which are not generally understood and have resulted in the past in depriving investors of the return of the money used in building irrigation works. The economic conditions have usually not been carefully studied in advance; generally the estimated cost of the completed system has been too small. While the engineers may have figured with considerable accuracy on certain structures, it has been found that the building of these necessary structures is only the beginning of the expenditure. The cost of promotion and of administration has frequently equaled that of engineering and construction proper; on top of this has usually been a lack of knowledge of water supply and of other conditions which have rendered many private enterprises unprofitable. The most difficult condition, however, has been that arising from the unforeseen delays and the impossibility of collecting promptly from the farmers the cost of the water. It has usually required years for them to subdue the soil and put it into highly productive condition. As a rule they have neglected to properly level and prepare it and the average crop production per acre has been ridiculously small at first as compared with the possibilities of the case.

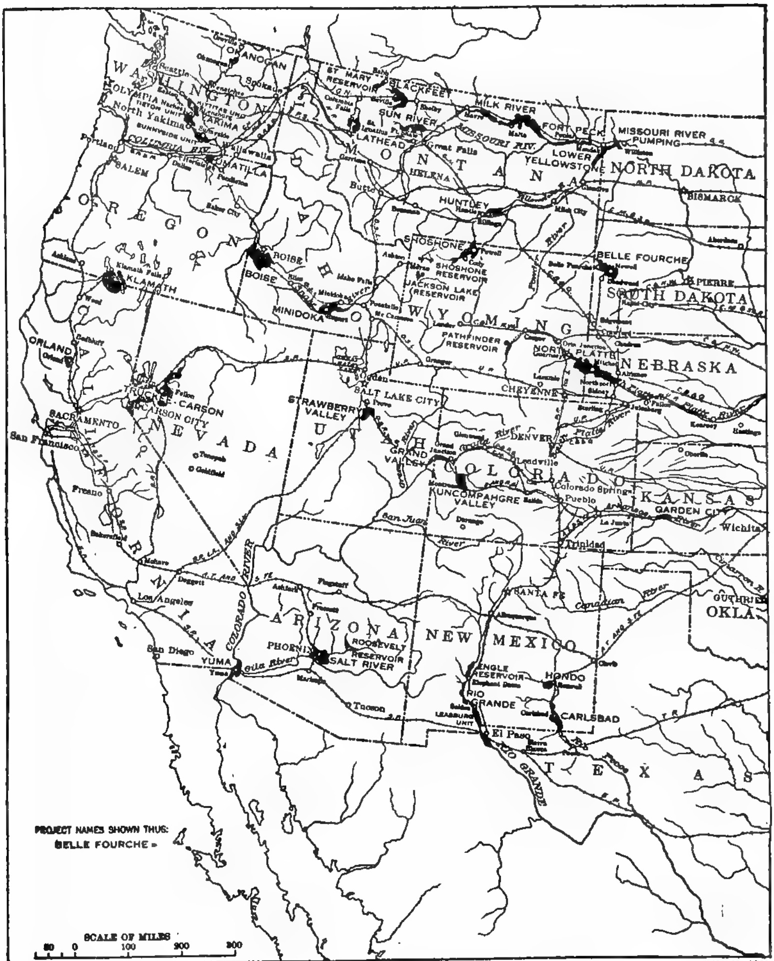
On every irrigated area there are usually to be found a number of persons who with skill and care have produced very large returns per acre, illustrating what might be done by their neighbors if all would exercise the same energy and follow the same methods. But the majority of the new comers do not do this at once and it requires many years of trial and the gradual elimination of the incompetent before the farmers, coming from all parts of the world, have acquired through individual experience the knowledge which enables them to produce highly profitable crops. Meantime the investors in these private works have been compelled to continue to operate and maintain them at large cost and have as a rule been unable to pay interest on their bonds, and have finally gone into bankruptcy during the time in which the farmers have learned how to irrigate successfully.

In the case of the work of the Government these delays, while injurious, are not as destructive as to private investors because the Government is not immediately dependent upon getting its money back or making large payments on interest on bonds. For this reason it is able to undertake and to carry through to successful completion enterprises which from their magnitude or intricacy would not be profitable to private capital.

The most serious of the complications which beset all enterprises of this kind are those which arise from the imperfections of the laws relating to the control of the waters in the streams. The distribution of these is under State authority and very few of the arid or semi-arid States have laws which are adequate to the conditions, most of the laws were patterned originally upon the common law practice of the humid states; the so-called "riparian rights," still lingering in portions of the arid West, practically forbid irrigation development. Even where the states have adopted the doctrine or theory of appropriation the practice has been so imperfect that the waters of most streams have been over appropriated to an extent many times that of the flood flow. The result is that in some of the states development is not only retarded but it has been ascertained that in some localities the amount spent in litigation exceeds that utilized in irrigation.

In the works built by the Government these matters of water rights are determined in advance of construction and on the basis of carefully conducted observations of river flow. Thus while it has been impracticable for private capital to delay to ascertain what are the conditions, it has usually been possible for the Government to select those localities where it is known that water is available and has not already been appropriated by others. For this reason the water rights obtained from the Government can be depended upon to actually yield water, while those purchased from private corporations have often been open to doubt.

Summing up the conditions, it may be said that the work of the Government in the conservation of waters and the use of these has not only stimulated private enterprise but has forced it to a high degree of attainment and has furnished a standard for construction and for adequacy of supply such as to materially improve the general conditions. It has used its resources in undertaking projects which otherwise could not have been handled, and in so doing has added materially to the wealth and prosperity of the nation and particularly of the sparsely settled states, not enriching any one small group of men, but enabling men of relatively small means to acquire homes and affording them an opportunity to become land owning citizens.



MAP NO. 13106 UNITED STATES RECLAMATION SERVICE JULY_1911

PRINCIPAL IRRIGATION PROJECTS
IN THE WESTERN UNITED STATES

THE RELATION OF THE CHEMICAL INDUSTRY TO THE ANNUAL FIRE LOSS OF THE UNITED STATES

J. Albert Robinson

Boston, Massachusetts

The people of the United States as a whole, born and bred as they have been in a country of apparently boundless natural resources, have failed to grasp the economic significance of the annual fire waste which is now giving deep concern to the few who are making careful studies and investigations of what is now recognized to be an unnecessary National affliction. Those who are born to great wealth and who accept such an environment without original thought do not usually realize the sources from which such wealth is drawn until a curtailment of the supply precipitates an investigation. The thought to which the American mind has long been a victim, namely, that our natural resources were unlimited, has resulted in the disregard of our created resources as well.

The destruction of our utilized resources by fire is increasing at such a rapid rate that the subject of its reduction must be deeply considered by every thinking man in the country. After a resume of the magnitude of this annual ash heap, should not every technical and manufacturing chemist here assembled, ask himself to what extent he has been a contributor to this profligate burning every year? And he should review the work that he has done to prevent this crime that means the inevitable impoverishment of the nation with a consequent demoralization perhaps in the particular industry with which he is identified. Perhaps the perspective of time and experience will make it clear that he has not done all that he might or all that he should.

The enormity of the following facts should sink deeply into the minds of every thinking person in the country. Losses recorded for the thirty-five years previous to 1907, not including forest, mine or marine fires, total the enormous sum of $4,906,619,240. Unrecorded losses, if obtainable, would materially increase these figures. These annual fire losses run from $64,000,000 in 1876 to $518,000,000 in 1906. In 1907, a normal year, our recorded losses were $215,084,709, and our estimated fire defense cost $241,401,191, or a total amount equalizing about fifty percent of the value of the new buildings erected that year in the entire country. In 1908, also a normal year, our ash heap cost $217,885,850 and the relations of defense cost and fire loss to new buildings remained about the same. Our contributions to fire that year were over 1¼ million dollars each day of the year, a sum equal to the operating expenses of our government including those of our army and navy, for the same year; and in 1909 we gave to fire over $25,000,000 more than was spent in that year for the same governmental functions.

According to the statistics of the Interior Department of the U. S. Government for the year 1910, the fire loss in the United States was more than $234,000,000. And in addition to the loss of this property these same statistics show that 1449 lives were sacrificed by fire and 5654 people were injured through this same agency. This tremendous drain upon the financial resources of this country, as indicated by these statistics, does not include any of the cost borne by the cities and villages, manufacturers and corporations throughout the country for the maintenance of the equipment to fight fire.

The loss for 1911 was also over $234,000,000. While there is no authentic record of all the outbreaks of fire in this country, it is generally known that the figures, if they could be presented, would serve as a monument to the carelessness of the nation. A carefully compiled record of the fires credited with causing a property loss of $10,000 or over in each instance shows that there were no less than 3410 such fires during 1911. This compares with 3225 fires in 1910.

An analysis and comparison of the reports of the Committee on Statistics of the National Board of Fire Underwriters for the years 1910 and 1911 show that the per capita loss for all the cities of 20,000 population and over in the United States was $2.39

in 1910 and $2.62 in 1911. A comparison with the per capita losses of foreign countries is most striking. Without going into the details of the number of cities and their population, which entered into this study, the average per capita losses for certain foreign countries were as follows:—England, 53 cents, Ireland 58 cents, Scotland 56 cents, France 81 cents, Germany 21 cents, Italy 31 cents, Russia $1.17. The statistics on which this data was based was doubtless sufficiently broad to be a fair indication of the rates of burning in the countries as a whole, and the average per capita loss for all of these foreign countries, as enumerated was sixty cents.

Many people, and even manufacturers and corporation managers, fail to give heed to the full significance of the facts and figures that have been quoted at length, owing to the prevalence of the foolish notion that the insurance companies pay this collossal tax. But how could they, and remain solvent? They are mere collectors and distributors of that portion of this tax which is represented by their policies. And although a factory and its contents may be fully covered by insurance, its owner cannot protect himself in event of fire against failure to complete orders of contracts; loss in the efficiency of his organization, (since skilled operators will accept positions with rival concerns during a shut-down of the burned-out plant); and loss of trade because no new business can be contracted until rebuilding is started.

Having considered broadly the fire loss of this country as a whole, it now becomes of especial interest to consider in more detail the relation of the chemical industry to the annual fire loss of the United States.

An analysis has been made of the losses from fire which occurred in thirty classes of techincal chemical and allied industries, during a period of ten years beginning January 1st, 1893 and ending December 31st, 1902. The figures used in this study were obtained from the carefully compiled annual records of The Chronicle Company which ceased publication of the Chronicle Fire Tables with the annual volume covering the statistics for the year 1902, and represent the most comprehensive and accurate figures of this kind that can be obtained.

List of the Thirty Branches of the Technical Chemical Industry Considered in the Statistical Study which Follows

1. Asphalt Works.
2. Bone, Ivory and Lampblack Factories.
3. Breweries.
4. Brick and Tile Works.
5. Cement, Lime and Whiting Works.
6. Charcoal and Coke Works.
7. Distilleries.
8. Drug and Chemical Works.
9. Fertilizer and Phosphate Works.
10. Gas Works.
11. Glass Works.
12. Glue Factories.
13. Hop Houses.
14. Lard, Tallow and Grease Melting Works and Refineries.
15. Malt Houses.
16. Oil Mills, Cotton Seed.
17. Oil—Miscellaneous Stills and Refineries.
18. Oil Tanks.
19. Paper and Pulp Mills.
20. Patent Medicine Factories.
21. Pottery Works.
22. Powder Mills.
23. Rubber Works. (Vulcanized Goods, etc.)
24. Soap and Candle Factories.
25. Starch Factories.
26. Sugar Refineries.
27. Sugar and Syrup Works.
28. Tanneries.
29. Tar, Pitch, Resin and Turpentine Factories.
30. White lead, Paint and Varnish Factories.

The following table shows the actual number of fires each year during this ten-year period, the total losses each year and the average loss per fire for each year in the thirty industries grouped together.

NO. OF FIRES AND LOSSES PER YEAR

Year	No. of Fires	Total Loss	Average Loss Per Fire
1893	497	$7,034,003	$16,165
1894	455	5,320,478	11,693
1895	527	6,176,064	11,719
1896	604	5,165,501	8,552
1897	580	5,801,530	10,003
1898	745	8,108,435	10,884
1899	781	5,342,620	6,841
1900	862	8,923,105	10,352
1901	820	8,749,865	10,671
1902	860	8,841,715	10,281

The following tables show in detail the number of fires, the losses, and the average loss per fire for each year of the decade, experienced by each of the thirty branches of the technical chemical industry which have been enumerated. They also show the total number of fires and total losses for the ten-year period and the average loss per fire determined from these totals.

While it is perfectly obvious that it is utterly impossible to gather together figures such as are contained herein with any absolute degree of accuracy, it does not necessarily follow that such a study will not have much of interest and even of considerable actual value. The general economic trend of the great fire waste in the chemical industry as a whole, and the broad relations between its branches, as regards the relative losses, number of fires, average losses, etc., cannot fail to show the chemical manufacturer that he had better look to his own fences if he wishes to keep in the vanguard of the march of progress.

The total loss figures, as given, are undoubtedly under estimates rather than over estimates, and the total losses today are unquestionably greater than in the decade during which the losses have been reported. This assumption is based on the fact that the aggregate average fire loss of the country is increasing steadily year by year, irrespective of the occasional great conflagration which may swell the loss figures for some individual year. Also the increase in the number and size of the various industries would suggest a normal relative increase in fire losses.

The total number of fires, as reported for each year and under each branch of the industry, is undoubtedly low, and the corresponding average losses per fire are probably high, but the general relations, as determined from the figures, are thought to express the actual facts fairly well.

There were probably many fires which occurred in plants equipped with automatic sprinklers where a small loss resulted that were never reported, but many of the industries, especially at the period represented by these figures, had no automatic protection and perhaps very little fire protection of any kind. Since this period, however, the automatic sprinkler has come into more general use in a number of the industries enumerated. While the aggregate losses, due to reasons previously mentioned, are undoubtedly greater today than ever, the average losses per fire are probably smaller than those given in the following tables.

There were 6771 fires included in this period which occurred in these thirty industries with an aggregate total loss of $70,584,111. The general average loss per fire for these industries was $10,424. The general average yearly rate of fires was 667 with a general average yearly loss of $7,058,411.

ASPHALT WORKS

Year	No. of Fires	Loss	Average Loss Per Fire
1902..................	17	$72,055	$4,328
1901..................	25	156,170	6,247
1900..................	13	22,245	942
1899..................	20	50,030	2,501
1898..................	10	7,900	790
1897..................	5	3,455	691
1896..................	3	25,700	8,567
1895..................	8	31,225	3,903
1894..................	9	28,880	3,209
1893..................	9	5,283	587
Totals.............	119	$402,943	$3,386

BONE, IVORY AND LAMPBLACK FACTORIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	2	$125	$63
1901	5	12,020	2,404
1900	4	7,100	1,775
1899	3	1,625	541
1898	1	250	250
1897	2	3,300	1,650
1896	4	4,250	1,063
1895	3	6,100	2,034
1894	3	24,600	8,200
1893	4	7,210	1,803
Totals	31	$66,580	$2,148

BREWERIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	57	$817,590	$14,344
1901	48	413,435	8,613
1900	51	326,625	6,404
1899	58	323,260	5,573
1898	55	555,555	10,101
1897	46	573,070	12,458
1896	57	479,555	8,413
1895	52	534,514	10,279
1894	45	435,401	9,675
1893	44	517,334	11,758
Totals	513	$4,976,339	$9,700

BRICK AND TILE WORKS

Year	No. of Fires	Loss	Average Loss Per Fire
1902	92	$719,895	$7,825
1901	80	493,070	6,163
1900	66	471,960	6,651
1899	71	279,430	3,936
1898	78	278,635	3,572
1897	46	246,845	5,366
1896	51	304,885	5,978
1895	53	703,565	13,275
1894	56	343,145	6,128
1893	66	837,121	12,684
Totals	659	$4,678,551	$7,100

CEMENT, LIME AND WHITING WORKS

Year	No. of Fires	Loss	Average Loss Per Fire
1902	28	$155,775	$5,564
1901	25	305,180	12,207
1900	39	637,450	16,345
1899	26	379,050	14,579
1898	37	324,255	8,764
1897	24	300,505	12,521
1896	19	89,865	4,730
1895	12	58,621	4,885
1894	12	97,050	8,088
1893	15	282,040	18,803
Totals	237	$2,629,791	$11,096

CHARCOAL AND COKE WORKS

Year	No. of Fires	Loss	Average Loss Per Fire
1902..................	5	$30,820	$6,164
1901..................	8	13,960	1,745
1900..................	2	40	20
1899..................	2	425	213
1898..................	5	47,500	9,500
1897..................	5	2,275	455
1896..................	1	15,000	15,000
1895..................	3	4,020	1,340
1894..................	3	5,650	1,883
1893..................	2	11,000	5,500
Totals.............	36	$130,690	$3,630

DISTILLERIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902..................	28	$119,095	4,253
1901..................	22	60,415	2,746
1900..................	18	74,420	4,134
1899..................	26	125,905	4,843
1898..................	28	334,475	11,945
1897..................	17	64,775	3,810
1896..................	19	186,675	9,825
1895..................	14	252,607	18,043
1894..................	12	90,500	7,542
1893..................	24	657,164	28,215
Totals.............	208	$1,966,031	9,452

DRUG AND CHEMICAL WORKS

Year	No. of Fires	Loss	Average Loss Per Fire
1902	60	$650,455	10,841
1901	65	705,885	10,860
1900	75	582,260	7,764
1899	72	353,355	4,908
1898	53	434,065	8,190
1897	36	118,605	3,295
1896	51	280,235	5,495
1895	34	259,280	7,626
1894	24	217,979	9,082
1893	22	328,103	14,914
Totals	492	$3,930,222	7,968

FERTILIZER AND PHOSPHATE WORKS

Year	No. of Fires	Loss	Average Loss per Fire
1902	23	$590.950	25,693
1901	26	320,585	12,330
1900	25	360,335	14,413
1899	29	284,620	9,814
1898	13	603,410	46,416
1897	21	579,340	27,588
1896	22	369,055	16,775
1895	10	278,125	27,813
1894	16	429,172	26,823
1893	20	433,024	21,651
Totals	205	$4,248,616	20,725

GAS WORKS

Year	No. of Fires	Loss	Average Loss Per Fire
1902	47	$76,565	1,629
1901	32	53,435	1,670
1900	54	65,365	1,210
1899	55	36,880	670
1898	42	124,890	2,974
1897	32	60,075	1,877
1896	24	134,475	5,603
1895	17	79,725	4,690
1894	19	42,227	2,222
1893	28	77,906	2,782
Totals	350	$751,543	2,147

GLASS WORKS

Year	No. of Fires	Loss	Average Loss Per Fire
1902	50	$439,840	8,797
1901	43	500,750	11,645
1900	61	359,805	5,900
1899	34	356,285	10,479
1898	33	894,315	27,100
1897	21	291,075	13,861
1896	15	364,560	24,304
1895	22	553,800	25,173
1894	15	408,250	27,216
1893	25	604,275	24,171
Totals	319	$4,772,955	14,962

GLUE FACTORIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	11	$136,005	12,364
1901	7	86,360	12,337
1900	3	975	325
1899	5	75,295	15,059
1898	5	142,325	28,465
1897	1	20	20
1896	4	202,025	50,506
1895	1	36,100	36,100
1894	1	24,000	24,000
1893	1	2,000	2,000
Totals	39	$705,105	18,079

HOP HOUSES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	8	$18,405	2,300
1901	8	19,075	238
1900	24	38,100	1,588
1899	29	50,200	1,731
1898	19	39,575	2,083
1897	19	34,100	1,795
1896	23	32,450	1,411
1895	29	43,750	1,509
1894	24	56,650	2,360
1893	14	29,000	2,071
Totals	197	$361,300	1,834

LARD, TALLOW AND GREASE MELTING WORKS AND REFINERIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	8	$277,595	34,699
1901	14	74,230	5,302
1900	15	267,920	17,861
1899	12	13,150	1,096
1898	8	35,575	4,872
1897	6	1,675	279
1896	11	10,625	966
1895	2	11,000	5,500
1894	3	11,000	3,667
1893	8	49,913	6,239
Totals	87	$752,683	8,652

MALT HOUSES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	17	$499,450	29,379
1901	7	43,085	6,155
1900	9	102,240	11,360
1899	6	119,240	19,873
1898	7	324,555	46,365
1897	19	219,175	11,536
1896	8	178,991	22,374
1895	9	354,123	39,347
1894	20	222,227	11,111
1893	8	254,099	31,762
Totals	110	$2,317,185	21,065

OIL MILLS, COTTON SEED

Year	No. of Fires	Loss	Average Loss Per Fire
1902	10	$243,600	24,360
1901	22	374,855	17,069
1900	12	670,165	55,847
1899	8	133,795	16,724
1898	11	189,800	17,255
1897	7	110,375	15,768
1896	6	245,850	40,975
1895	3	204,000	68,000
1894	3	315,050	105,017
1893	1	500	500
Totals	83	$2,487,990	29,976

OIL—MISCELLANEOUS STILLS AND REFINERIES

(Not including Cotton Seed, Linseed and Lubricating Oils)

Year	No. of Fires	Loss	Average Loss Per Fire
1902	70	$421,415	6,020
1901	43	771,270	17,937
1900	24	138,345	5,723
1899	31	147,035	4,743
1898	28	198,065	7,074
1897	38	190,260	5,007
1896	33	300,400	9,043
1895	21	253,355	12,065
1894	17	96,388	5,670
1893	26	467,694	17,988
Totals	331	$2,984,227	9,016

OIL TANKS

Year	No. of Fires	Loss	Average Loss Per Fire
1902	48	$186,955	3,895
1901	50	240,135	4,803
1900	102	2,108,630	20,673
1899	48	139,255	2,901
1898	66	351,160	5,321
1897	41	168,155	4,101
1896	55	112,500	2,045
1895	33	103,250	3,129
1894	15	149,025	9,935
1893	14	76,100	5,436
Totals	472	$3,635,165	7,702

PAPER AND PULP MILLS

Year	No. of Fires	Loss	Average Loss Per Fire
1902	73	$639,225	8,620
1901	70	1,752,275	25,033
1900	62	1,128,670	18,204
1899	44	403,015	9,159
1898	42	708,700	16,874
1897	35	895,150	25,576
1896	32	178,410	5,575
1895	37	649,136	17,544
1894	38	612,340	16,114
1893	45	878,529	19,523
Totals	478	$7,845,450	16,413

PATENT MEDICINE FACTORIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	6	$9,150	1,525
1901	14	34,930	2,495
1900	10	155,475	15,548
1899	14	58,620	4,187
1898	7	22,580	3,226
1897	13	53,850	4,142
1896	11	46,480	4,225
1895	7	26,605	3,801
1894	9	22,201	2,467
1893	8	31,074	3,884
Totals	99	$460,965	4,656

POTTERY WORKS

Year	No. of Fires	Loss	Average Loss Per Fire
1902	29	$578,350	19,943
1901	22	401,905	18,268
1900	19	236,500	12,447
1899	16	74,630	4,664
1898	20	82,030	41,015
1897	16	202,165	12,635
1896	7	307,500	43,929
1895	18	263,165	14,620
1894	12	178,800	14,900
1893	15	227,375	15,158
Totals	174	$2,652,420	15,244

POWDER MILLS

Year	No. of Fires	Loss	Average Loss Per Fire
1902	21	$120,700	5,748
1901	10	44,700	4,470
1900	7	23,800	3,400
1899	7	15,400	2,200
1898	20	77,250	3,863
1897	8	264,100	33,013
1896	14	53,950	3,854
1895	4	8,500	2,125
1894	2	4,000	2,000
1893	4	51,000	12,750
Totals	97	$663,400	6,839

RUBBER WORKS (VULCANIZED GOODS, ETC.)

Year	No. of Fires	Loss	Average Loss Per Fire
1902	10	$36,930	3,693
1901	17	32,125	1,890
1900	14	50,785	3,628
1899	10	42,485	4,249
1898	14	634,485	45,320
1897	14	84,645	6,046
1896	7	45,800	6,543
1895	12	63,175	5,281
1894	8	4,200	525
1893	4	6,085	1,521
Totals	110	$1,000,715	9,097

SOAP AND CANDLE FACTORIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	13	$39,585	3,045
1901	14	30,780	2,199
1900	20	166,310	8,316
1899	26	104,845	4,033
1898	18	376,010	20,889
1897	14	19,040	1,360
1896	19	231,590	12,189
1895	25	209,455	8,378
1894	13	42,475	3,267
1893	20	110,498	5,525
Totals	182	$1,330,588	7,311

STARCH FACTORIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	6	$4,435	739
1901	9	683,560	75,951
1900	3	2,575	858
1899	5	9,700	1,940
1898	7	506,800	72,400
1897	2	36,500	18,250
1896	3	8,700	2,900
1895	6	206,200	34,367
1894	1	700	700
1893	0		
Totals	42	$1,459,170	34,742

SUGAR REFINERIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	2	$50,090	25,045
1901	8	70,350	8,794
1900	1	25	25
1899	3	61,865	20,622
1898	1	55,000	55,000
1897	3	62,500	20,833
1896	2	70,400	35,200
1895	2	63,650	31,825
1894	0		
1893	2	233,166	116,583
Totals	24	$667,046	27,794

SUGAR AND SYRUP WORKS

Year	No. of Fires	Loss	Average Loss Per Fire
1902	36	$206,890	5,747
1901	28	199,905	7,139
1900	18	301,865	16,770
1899	22	156,285	7,104
1898	26	267,025	10,270
1897	11	285,215	25,929
1896	13	244,930	18,841
1895	10	246,900	24,690
1894	10	807,574	80,757
1893	3	51,967	17,322
Totals	177	$2,768,556	15,642

TANNERIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	36	$1,043,700	28,992
1901	43	396,880	9,207
1900	40	1,028,435	25,711
1899	38	1,077,340	28,351
1898	28	369,420	13,193
1897	35	676,015	19,315
1896	41	237,750	5,799
1895	33	454,465	13,772
1894	23	327,750	14,250
1893	32	333,080	10,409
Totals	349	$5,964,835	17,091

TAR, PITCH, RESIN AND TURPENTINE FACTORIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	9	$19,865	2,207
1901	8	5,900	738
1900	19	31,750	1,671
1899	9	24,800	2,755
1898	24	31,500	1,313
1897	11	41,090	3,735
1896	17	16,030	943
1895	17	29,155	1,715
1894	16	16,150	1,009
1893	24	47,850	1,994
Totals	154	$264,090	1,715

WHITE LEAD, PAINT AND VARNISH FACTORIES

Year	No. of Fires	Loss	Average Loss Per Fire
1902	38	$636,205	16,742
1901	47	452,640	9,631
1900	52	562,935	10,826
1899	52	444,800	8,554
1898	39	91,330	2,342
1897	32	214,180	6,693
1896	32	387,665	12,115
1895	30	188,498	6,283
1894	26	307,094	11,811
1893	49	423,613	8,645
Totals	397	$3,708,960	9,342

The following table shows the number of fires experienced during the ten-year period in each of the thirty branches of the technical chemical industry enumerated, in the order of their frequency.

FREQUENCY OF FIRES BY CLASSES

Class	No. of Fires
1. Brick and Tile Works	659
2. Breweries	513
3. Drugs and Chemical Works	492
4. Paper and Pulp Mills	478
5. Oil tanks	472
6. White Lead, Paint and Varnish Factories	397
7. Gas Works	350
8. Tanneries	349
9. Oil Stills and Refineries (Miscellaneous)	331
10. Glass Works	319
11. Cement, Lime and Whiting Works	237
12. Distilleries	208
13. Fertilizer and Phosphate Works	205
14. Hop Houses	197
15. Soap and Candle Factories	182
16. Sugar and Syrup Works	177
17. Pottery Works	174
18. Tar, Pitch, Resin and Turpentine Factories	154
19. Asphalt Works	119
20. Malt Houses	110
21. Rubber Works	110
22. Patent Medicine Factories	99
23. Powder Mills	97
24. Lard, Tallow and Grease Melting Works	87
25. Cotton Seed Oil Mills	83
26. Starch Factories	42
27. Glue Factories	39
28. Charcoal and Coke Works	36
29. Bone, Ivory and Lampblack Factories	31
30. Sugar Refineries	24

The following table shows the total losses during the ten-year period in each of the thirty branches of the technical chemical industry enumerated, in the order of their magnitude.

LOSSES BY CLASSES

Class	Loss
1. Paper and Pulp Mills	$7,845,450
2. Tanneries	5,964,835
3. Breweries	4,976,339
4. Glass Factories	4,772,955
5. Brick and Tile Works	4,678,551
6. Fertilizer and Phosphate Works	4,248,616
7. Drug and Chemical Works	3,930,222
8. White Lead, Paint and Varnish Factories	3,708,960
9. Oil Tanks	3,635,165
10. Oil. Miscellaneous Stills and Refineries	2,984,227
11. Sugar and Syrup Works	2,768,556
12. Pottery Works	2,652,420
13. Cement, Lime and Whiting Works	2,629,791
14. Cotton Seed Oil Mills	2,487,990
15. Malt Houses	2,317,185
16. Distilleries	1,966,031
17. Starch Factories	1,459,170
18. Soap and Candle Factories	1,330,588
19. Rubber Works	1,000,715
20. Lard, Tallow and Grease Melting Works & Refineries	752,683
21. Gas Works	751,543
22. Glue Factories	705,105
23. Sugar Refineries	667,046
24. Powder Mills	663,400
25. Patent Medicine Factories	460,965
26. Asphalt Works	402,943
27. Hop Houses	361,300
28. Tar, Pitch, Resin and Turpentine Factories	264,090
29. Charcoal and Coke Works	130,690
30. Bone, Ivory and Lampblack Factories	66,580

The following table shows the average loss per fire, during the ten-year period, in each of the thirty branches of the technical chemical industry enumerated, in the order of their magnitude.

AVERAGE LOSS PER FIRE BY CLASSES

Class	Average Loss Per Fire
1. Starch Factories	$34,742
2. Cotton Seed Oil Mills	29,976
3. Sugar Refineries	27,794
4. Malt Houses	21,065
5. Fertilizer and Phosphate Works	20,725
6. Glue Factories	18,079
7. Tanneries	17,091
8. Paper and Pulp Mills	16,413
9. Sugar and Syrup Works	15,642
10. Pottery Works	15,244
11. Glass Works	14,962
12. Cement, Lime and Whiting Works	11,096
13. Breweries	9,700
14. Distilleries	9,452
15. White Lead, Paint and Varnish Factories	9,342
16. Rubber Works	9,097
17. Oil. Miscellaneous Stills and Refineries	9,016
18. Lard, Tallow and Grease Melting Works & Refineries	8,652
19. Drug and Chemical Works	7,968
20. Oil Tanks	7,702
21. Soap and Candle Factories	7,311
22. Brick and Tile Works	7,100
23. Powder Mills	6,839
24. Patent Medicine Factories	4,656
25. Charcoal and Coke Works	3,630
26. Asphalt Works	3,386
27. Bone, Ivory and Lampblack Factories	2,148
28. Gas Works	2,147
29. Hop Houses	1,834
30. Tar, Pitch, Resin and Turpentine Factories	1,715

While the foregoing tables have shown the actual losses, number of fires, and average loss per fire in each of the thirty branches of the technical chemical industry, and vividly illustrated the great toll that the chemical industry is paying to the fire fiend, they have not brought out facts in regard to the actual rate of burning in the various industries. They show clearly those classes which are prone to suffer a greater or less degree of loss in the fires which occur, but they do not show which industry would appear to be the most hazardous or suffer the greatest drain on the resources of that particular industry. To get these facts we should make comparisons with the actual number of plants employed in any given branch of the industry and the total values of these plants in these branches. Such comparisons have been made in following tables.

The following table is based upon information gathered during the 12th census of the United States in the reports on manufactures. The values include building, machinery, tools and implements.

NO. OF PLANTS AND VALUATION IN VARIOUS INDUSTRIES

Class	No. of Factories	Total Value	Average Value
Bone, Ivory and Lampblack Factories	15	$542,793	$36,186
Breweries	1509	195,631,283	129,643
Brick and Tile Works	5422	38,345,021	7,072
Drug and Chemical Works	459	39,621,776	86,322
Fertilizer and Phosphate Works	422	16,022,778	37,969
Gas Works	877	435,276,807	496,325
Glass Works	355	31,201,576	87,908
Glue Factories	61	1,580,002	25,900
Malt Houses	146	17,788,931	121,842
Cotton Seed Oil Mills	369	21,200,788	57,455
Paper and Pulp Mills	763	95,791,250	125,545
Rubber Works	262	11,093,119	42,340
Soap and Candle Factories	558	13,169,030	23,600
Starch Factories	124	6,406,813	51,667
Tanneries	1306	35,807,651	27,418
Tar, Pitch, Resin and Turpentine Works	425	1,274,626	3,000

The following table expresses the relation between the average number of fires per year, during the last five years of the ten-year period, in the sixteen branches of the technical chemical industry enumerated, and the number of plants reported in each industry according to the previous table, given in the order of the rate of burning.

RATE OF BURNING

(An average of one fire occurred for the number of factories indicated)

Class	Average No. Fires per Year During Five-Year Period	Total No. of Plants	No. of Plants per Fire
1. Bone, Ivory and Lampblack Factories	3	15	5
2. Drug and Chemical Works	65	459	7
3. Glass Works......................	44.2	355	8
4. Glue Factories....................	6.2	61	10
5. Paper and Pulp Mills..............	58.2	763	13
6. Malt Houses.......................	9.2	146	16
7. Fertilizer and Phosphate Works.....	23.2	422	18
8. Gas Works.......................	46	877	19
9. Rubber Works....................	13	262	20
10. Starch Factories..................	6	124	21
11. Breweries........................	53.8	1509	28
12. Cotton Seed Oil Mills..............	12.6	369	29
13. Soap and Candle Factories.........	18.2	558	30
14. Tar, Pitch, Resin and Turpentine Works..........................	13.8	425	31
15. Tanneries........................	37	1306	35
16. Brick and Tile Works	77.4	5422	70

The following table expresses the relation between average loss per fire during the last five years of the ten-year period, in the sixteen branches of the technical chemical industry enumerated, and the average value of the plants in each industry, given in the order of the average percentage loss on each per fire.

PERCENTAGE LOSS PER FIRE

Class	Average Loss per Fire During the Five-Year Period	Average Value of Plants	Percentage Loss per Fire
1. Brick and Tile Works	5,796	7,072	82
2. Starch Factories	40,235	51,667	78
3. Tanneries	21,166	27,418	77
4. Tar, Pitch, Resin and Turpentine Works	1,649	3,000	55
5. Glue Factories	14,225	25,900	61
6. Fertilizer and Phosphate Works	18,620	37,969	49
7. Cotton Seed Oil Mills	25,591	57,455	45
8. Soap and Candle Factories	7,885	23,600	33
9. Rubber Works	12,259	42,340	29
10. Glass Works	11,543	87,908	13
11. Paper and Pulp Mills	15,917	125,545	13
12. Malt Houses	23,665	121,842	11
13. Drug and Chemical Works	8,388	86,322	9
14. Breweries	9,057	129,643	7
15. Bone, Ivory and Lampblack Factories	1,408	36,186	4
16. Gas Works	1,553	87,908	Less than 1

Prevention is the keynote of the situation. The tendency of all humanitarian endeavor today is toward prevention of evil. In sociology we no longer rely upon efforts to reform the hardened criminal; we have turned our attention to the child to save him from the ways of crime. In medicine we no longer only drug and physic the sick; we teach the well how to keep from getting sick. The basic idea of modern sanitation also is prevention rather than cure. Although there has been a popular idea that the insurance companies profit by and welcome great fires, as a matter of fact the most marked feature in the insurance field in the last decade has been the growth of the preventive idea, the deliberate attempt of the companies to combat the dangers against which they have insured. It may be that in so doing their motives have not been entirely altruistic—that they realize that profits are made not from high-priced risks but from the so-called "improved risks," risks where losses are extremely unlikely to occur.

But whatever their motives the fact remains that the companies in every branch of the insurance field are doing everything in their power to prevent the casualties insured against. The burglar insurance companies do not seek to shield the thief, nor fidelity companies the defaulter. We find the fidelity companies fighting the race tracks and other sources of temptation, the burglary companies fighting crime, the liability companies fighting accidents, the life companies fighting disease. The fire insurance companies have developed engineering bureaus maintained by specialists in the art of proper construction and protection, and experts capable of solving the problem of safeguarding the common and special fire hazards encountered in all lines of manufacture and business. Help and advice are given freely at all times to those who seek it. A great laboratory is maintained for the purpose of examining and passing upon the integrity of fire prevention apparatus and the regulation and approval of apparatus involving the use of hazardous materials.

It is, therefore, a pertinent question for us to ask,—"What are the manufacturing chemists of the country doing in the way of prevention?" The New York Capitol cost $28,000,000 but it did not contain a water pail, a foot of fire hose, or a fire alarm box. Such short-sightedness is incomprehensible now, although it required a costly fire to reveal the absence of the most rudimentary fire-fighting appliances. How many, many other public buildings, upon which millions have been lavished, are in the same condition? And are any manufacturers taking such a chance?

Innumerable means have been devised from time to time to minimize this chance, involving the use of both automatic and hand-operated devices. It is needless to say that the former are, at the inception of a fire, much the more valuable by reason of the fact that when properly operative they act as soon as the fire has made its presence distinctly manifest. The record of sprinklered risk fires, as shown by the carefully compiled fire records of the National Fire Protection Association, show that in 12180 fires occurring in properties equipped with automatic sprinklers during the past sixteen years, 63.63 percent were practically or entirely extinguished by the operation of the sprinklers.

There were five percent in which the automatic equipment proved unsatisfactory, and in 31.37 percent of the fires the sprinklers held the fire in check. More than three-fourths of the failures were due to the water being shut off, a generally defective equipment and unsprinklered portions, defective water supplies and exposure fires.

Remarkable as is this record of success in controlling fire through the action of automatic sprinklers, it must not be assumed that there is no limitation to their power of accomplishment in fire extinguishment, as a reference to the figures given above will show that something over thirty-one percent of the fires were simply held in check by the sprinklers until other means of fighting the fire could be utilized, and this fact emphasizes the necessity for always being prepared for any untoward condition of automatic equipment, by providing auxiliary means to control the flame when from any cause the sprinklers fail to completely extinguish it, for even with a perfectly satisfactory installation we are often confronted with conditions due to accident or carelessness which, for a time at least, may entirely or partially disable the equipment after it has gone into operation.

From figures compiled by a manufacturer of automatic equipment it was shown that before the more general introduction of automatic sprinklers in factories, the average cost per fire was $7,361, while under automatic sprinkler protection the average cost per fire in 13,476 cases covered by their records, amounted to but $277.26 each.

The fact must not be overlooked, however, that in several kinds of chemical industries the use of automatic sprinklers does not prove practical owing to the nature of construction, corrosive action of fumes and vapors, and damageability of the materials used and their liability to explode. To such plants, earnest thought should be given as to the best methods of protection against fire, and advice should be sought from well qualified fire protection engineers which is freely given by the Underwriters having jurisdiction.

We, however, must strike deeper than fire protection to attain real prevention. Medicine, after the disease has become malignant, can only be palliative. To cure the disease the fundamental causes must be removed. Our great fire losses are due to two fundamental defects—improper construction and neglect of common and special hazards. To these must be added our national trait of endemic carelessness and a tendency to neglect proper housekeeping.

The common errors of construction, such as unprotected floor openings, undivided areas of great magnitude and lack of protection against exposure, are too well recognized today to need further elucidation in this paper, and the factories of the future will more and more be built of fire-resistive construction.

The actual causes of fire, however, are often overlooked and do not receive the attention that they should. As we learn mostly from experience a study of the causes of fires which occur in a given industry offers the best source of information as to preventive measures against their reoccurrence. The various branches of the chemical industry suffer their share from the common causes of fire which are prevalent in all classes of property irrespective of the particular occupancy or industry that may be carried on therein. These common causes of fire are due to heating and lighting systems, transmission of power, boilers and fuel, smoking and matches, locomotive sparks, lightning, oily waste and similar materials liable to spontaneous ignition, sweepings and rubbish, general uncleanliness and poor housekeeping, incendiarism and exposure fires. They are largely due to inexcusable ignorance or criminal carelessness.

The so-called special hazard fires, or fires due directly to the occupation or processes carried on within the premises, should receive the most careful consideration. It is such fires that differentiate one class of industry from another in the eyes of the underwriter so that certain classes are found in his experience to be much more hazardous than others. It is from such fires, therefore, that the manufacturing chemist can well give more thought. Revolutionary changes and improvements in the processes of manufacture have frequently been brought about in the past through an endeavor to improve the fire hazards of that process.

In order to demonstrate the instructive points that may be found in such a study, the following abstracts of fire causes are taken at random from fire reports in the files of the National Fire Protection Association covering fires of a special hazard or process origin in establishments manufacturing pharmaceutical general and heavy chemicals.

1. There were four dry boxes about two feet square and six feet high for drying various pharmaceutical preparations in wooden trays set six inches apart, none of which extended the length of the four boxes. A block supporting the radiator was found tipped over and the pipes came in contact with woodwork. There was a tray at bottom reserved for catching compounds spilled from trays. Fire undoubtedly caused by contact of steam pipes with woodwork.

2. Dry room contained twenty-four frame dry closets, twelve on each side of the room, each separated by a frame partition and heated by steam pipes on iron to a temperature of approximately 200 degrees Fahrenheit. The dry closets were arranged with slats on the sides to hold light wooden trays with canvas or muslin fastened to these to hold the paste mixtures for drying. Closets where fire occurred contained a mixture of charcoal and water and a mixture of oxgall and pancreatin. Fire thought to have been caused by the trays or cloth coming in contact with the steam pipes.

3. Closet of light wood construction with a large number of trays with wooden sides and canvas bottoms. Drier contained quinine tablets and no combinations liable to spontaneous ignition. Steam pipes probably responsible.

4. Steam pipes in contact with woodwork of small frame bismuth dry room.

5. Frame enclosed metal lined rack drying closet, drying medical paste.

6. Steam pipes in metal clad drier box in a medicine factory was cause of fire.

7. Fire occurred in bark grinding mill, caused by a nail in the material.

8. Fire occured in drug grinding mill, caused by some foreign substance. Spark ignited the powdered stock.

9. Alcohol was spilled by the night watchman in the fluid room of a pill factory, and the vapor was ignited by his lantern.

10. Watchman went to drug vault for some kerosene and his lantern ignited benzine vapors.

11. While filling a bottle from a tank of turpentine in a dark room, the operator lighted a match and accidentally ignited turpentine on the wooden support for the tank.

12. Half a gallon of ether in a bottle was being heated on a steam bath. Bottle burst and vapors were ignited by a gas jet nearby.

13. Oily waste accidentally ignited in quinine extracting room.

14. Explosion occurred in alcohol refining still.

15. Fire occurred in a plant manufacturing hospital supplies, in the acid room, due to explosion of nitric acid fumes probably in connection with fumes of ammonia.

16. Fire occurred in stock room due to spontaneous ignition of a bag of cascara bark.

17. Fire caused by the explosion of a retort used for distilling.

18. Compound consisting mainly of creosote, which was being heated in a cast-iron kettle heated by wood fire, boiled over and ignited.

19. Fire occurred in a tablet room having a dust collector box with metal pipe exhaust to roof, due to friction of pulley on blower fan.

20. An employee pouring ether from small cylinder into a can or other receptacle spilled some of the ether. The liquid ran along a table and struck the hot electric soldering iron and this iron was hot enough to ignite the vapor of the ether. An explosion occurred, followed by fire.

21. Fire occurred in a wood alcohol manufacturing plant due to the jamming of one of the wheeled iron cages containing charcoal fresh from the furnaces, against the top or side of the iron cooler into which the charcoal was being run. It was supposed that one of the rails had sprung which would account for the jamming. Although every effort was made by the employees to force the car far enough into the cooler to enable them to close the air tight door, they were unable to do so owing largely to the intense heat thrown off by the burning charcoal.

22. Workmen were engaged in removing a carload of chlorate of soda and depositing it in a frame warehouse by means of a

wheel-barrow with iron rimmed wheel. Some of the chlorate sifted through the kegs and men noticed a fire creeping along the floor where a barrow had passed.

23. A case contained bottles of hydrochloric, nitric and sulphuric acid. One of these became broken and the excelsior packing was ignited.

24. A small smount of aniline oil was being distilled in an ordinary can over a bunsen flame under a hood in the laboratory of a chemical works. The solder in bottom of can melted and allowed the boiling liquid to escape. This was ignited and caused a fire.

25. A carboy of sulphuric acid was broken and hay packing became ignited.

26. Wood alcohol plant totally destroyed through negligence in taking proper care of the charcoal after removal from the retorts. There was about 300 bushels of charcoal stored in bins inside of building, and this ignited.

27. Fire thought to have been caused by a leak in the fuel oil pipe which fed burners under caustic soda furnaces. The oil flowed into the furnace and was ignited.

28. An iron pan set over a brick furnace fired with hard coal was used to boil nitrite of soda. The contents boiled over and a vigorous fire ensued. Hot coals were scattered about the room and a large wooden rotary drier some distance away was ignited.

29. Fire occurred from unknown cause in a warehouse containing chlorates of potash and soda and saltpetre. The account given by the investigator is of interest.

"Across the street there were a number of old dwellings and the occupants were awakened by a hissing sound attending a fierce fire. The windows and openings of the warehouse were soon blown out. Repeated explosions followed with varied force and noise, which could be heard several blocks away. Fortunately, the roof was broken by one of the first explosions and this afforded a vent, directing the effect of the explosions upward.

30. Explosions during combustion among chlorates or nitrates wherever present are to be expected even from combination with the wood of the kegs alone; the result being the evolution of

immense volumes of oxygen from the salts, producing rapid combustion; and where bodies of smoke arise intermittingly, an explosive mixture is formed by the heated oxygen with the gases and unburned carbon in the smoke. The violence of the detonations depends on the proportions of oxygen and other gases. The firemen stated that the water at times seemed to add to the explosions. This latter effect results from water in the form of spray being thrown on such a fire; the heat being so intense as to cause decomposition of the water with sharp explosive effect."

31. Fire occurred in still room of an acetone plant, due to an explosion from unknown cause.

32. Fire caused by the boiling over of a kettle of rosin through lack of attention on the part of the night watchman.

33. Fire occurred from unknown cause in a bismuth drying building.

34. Employee was cleaning out a metal tank which had contained a hydro-carbon oil. He had an electric lamp with extension cord in tack. A short circuit occurred owing to a defect in the cord and a slight explosion followed.

35. A kettle of rosin boiled over causing a fire.

36. Fire evidently started from friction around the driving gear of a steam heated sodium nitrite drier, and heat became sufficient to explode contents of rotary with considerable violence.

37. In the sulphur burning room of a plant manufacturing hyposulphite of soda, fire was caused by melted sulphur which ran through cracks in the floor and ignited loose sulphur scattered about underneath.

38. An employee was placing granulated chlorate of potash on trays previous to placing them in steam heated driers, when a blaze occurred on one of the trays and spread so rapidly that employee was burned while making his escape.

39. Fire occurred in an electrolytic cell in the manufacturing of bleaching powder. A new cell had been put in operation about an hour before the fire and in some unknown way it became overheated. The paraffin oil contained therein boiled out, ignited, and set the frame cell-house on fire.

40. An explosion occurred in grinding mill of a sulphur plant caused by foreign substance in the mill.

41. An explosion occurred in the elevator leg of a sulphur plant caused by the friction of the elevator against the inclined leg. Fire ensued and frame mill adjoning the flour chamber was destroyed.

42. Retort house of a sulphur plant destroyed by fire presumably due to a defective flue.

43. Fire occurred in the roll stick department of a sulphur plant due to a defective still which ignited the low roof trusses of building.

44. Fire occurred in the retort and still house of a sulphur plant while still was in operation, probably due to escaping gas through connections from retorts.

45. Fire caused at a chemical works by the process of lead burning with an oxy-hydrogen flame. A new crystallizing tank was being lined with lead. A wooden post at corner where lining was being jointed became ignited.

46. Fire occurred in the finishing room of thorium nitrate plant. The finishing process consisted in boiling the nitrate of thorium down in open vessels over a gas fire. Over these vessels was constructed a wood ventilating hood for carrying off fumes. The attendant discovered that the hood was in flames, and the supposition was that the wooden hood had become kiln dried and ignited from the heat.

47. Fire in a saltpetre works started in room where saltpetre was dried in shallow iron vats with steam coils underneath. A workman was installing a new vat and spark from hammer flew a few feet into adjoining vat, igniting the saltpetre. Fire spread very rapidly to other vats.

48. A camphor still was located in a separate room and discharged through a pipe into a room called the camphor chamber. Several days before the fire, a damaged lot of camphor was returned from a celluloid factory to be refined. This was put through the still and was probable that nitric acid fumes were carried into chamber with the camphor vapor, settled on walls of chamber, and finally oxidized and ignited the camphor deposited there.

49. Fuel oil used to supply burners for borax roasters escaped and became ignited by flame at burners.

50. Fire resulted from the explosion of a grease still used in the manufacture of stearic acid and glycerine. Carry-off pipe was found to be clogged with the deposit, and live steam was injected. It is supposed that an excess pressure accumulated in the still which ruptured the still. Room was filled with tar and vapor and was ignited from the fire under steam boiler nearby.

51. Fire caused by cold cream boiling over in a laboratory manufacturing perfumes and toilet articles.

52. The boiling kettles used in the manufacture of aniline blue were heated by coal. One of these kettles boiled over and aniline oil took fire at once, causing a hot fire. There were two occurrences of this sort at one plant which caused a loss of $1,500.00.

"Find out the cause of this effect:
Or, rather say, the cause of this defect,
For this effect defective comes by cause."
Hamlet 11:2

One cannot study these miscellaneous effects, chosen at random from a large source of similar fires in the varied classes of chemical industries involved, without being greatly impressed with the fact that most of these defects were readily preventable and that many of them were due to gross carelessness.

The few fires of unknown chemical origin that have been quoted, and a larger number of fires which are constantly occurring in bleach and dye works and other manufactories using products of the chemical industry, that have apparently been due to the presence of the dyes or chemicals, suggest the possibility of valuable study and research on the part of chemists to eliminate these conditions.

Having stated the national scope and economic significance of the annual tremendous loss of created and natural resources by fire, and analyzed in detail the magnitude of this loss in the chemical industries, it is hoped that each member of the Eighth International Congress of Applied Chemistry will become sufficiently interested in this most vital subject, to become an ardent disciple of fire prevention and fire protection and to give greater thought and study to ways and means of applying such remedies as may seem desirable to his own needs.

Franklin H. Wentworth, Secretary of the National Fire Protection Association, which is an organization and technical body of national scope and broad membership, making the standards under guidance of which the fire waste may be checked, and educating the people in the observance of those standards and pointing out the grievous economic penalties for ignoring them, stated a great truth in a recent notable address:—

"Our civilization grows daily more complex. Every man's life is becoming more inextricably linked with the lives of others. An injury to one is increasingly an injury to all. Out of a proper realization of these facts is coming a larger sense of civic responsibility. As citizens of a common country, and brothers of a great national family, we may some day evolve a civilization in which there shall be no waste and in which the thought of the common good shall be the profoundest impulse in the hearts of our people."

THE CONSERVATION MOVEMENT IN WISCONSIN

By Charles R. Van Hise; Forests by E. M. Griffith
Madison, Wisconsin

The Conference of the Governors at the White House in May, 1908, upon the conservation of natural resources in the United States will by future generations be regarded as one of the great historical events of the nation. For many years the voice of the scientific man had here and there been raised for conservation, but his voice was a voice in the wilderness. President Roosevelt made the voice of conservation the voice of the nation.

Following the White House Conference, the President appointed a national conservation commission and many of the governors of the states appointed state conservation commissions. Governor James O. Davidson in Wisconsin, by executive act without authority of the legislature appointed a State Conservation Commission. This commission was made effective through a letter by the governor to the heads of the various departments of the state, requesting them to co-operate with the commission.

The Wisconsin commission has made two reports which by the governor were presented to the legislature, the first in 1909, and the second in 1911. The legislature of the latter year placed the conservation commission on a legal basis and made a small appropriation for its work.

The Wisconsin conservation commission early adopted the policy of confining its reports to specific matters regarding which the commission thought the time was ripe for legislative enactment or for a public movement. Upon such subjects brief papers by specialists were prepared describing the situation and pointing out the remedies. The commission, using these papers as a foundation, made definite recommendations to the governor. A surprisingly large proportion of these recommendations have been enacted into law.

THE WATER POWERS

Since the admission of the state of Wisconsin to the Union until 1909, it had been the practice of the legislature to grant franchises for the construction of dams, nominally to improve navigation but really for the development of water powers, upon the request of any individual or company, without condition, except the protection of such recognized public rights as navigation, maintenance of runways for fish, etc. Many of these franchises included the right of condemnation in order to give the necessary flowage areas.

The conservation commission in its first report recommended that thereafter franchises for water powers be granted under a general statute; that the issuing of such franchise be placed with the railway commission, or similar board, under conditions provided by the general statute; that such franchise be in the nature of a lease for a long period of years, with privilege of renewal on reasonable terms; and that an equitable rental charge, low at first, be imposed.

The legislature of 1909, at least partly in consequence of the report of the conservation commission, refused to grant any special franchises for the construction of dams, and appointed a special recess committee to investigate the subject of water powers and report a bill to the succeeding legislature.

In the report of the conservation commission for 1911 there was proposed as an alternative method of leasing water power, indeterminate franchises carefully safeguarding the public interests, and under the principles of the general public utilities act. In case either of rental for a definite period or an indeterminate lease, the rate of rental was to be low at first and to be readjusted at reasonable periods.

The legislature of 1911 refused to grant any special franchises for water powers, but enacted a general law [1] relating to the construction and maintenance of dams across navigable waters and granting franchises for the improvement of navigation and the development of hydraulic power. The act provided for granting franchises for the term of twenty years, with the right of continuance of such franchises for two further terms of ten years each, subject to readjustment of the charge per horse power. The franchise fee was to be five per cent of the franchise value of the water power utilized, with the provision that such charge be not less than ten cents nor more than two dollars per horse power per annum. The administration of the water power law was placed upon the railway commission.

---

[1] Chapter 652, Wisconsin Session Laws of 1911.

The law declared that "all energy developed or undeveloped on the navigable waters of this state is subject to the control of the state for the public good and also the beneficial use and natural energy of the natural waters of this state for all public purposes are held by the state in trust for all the people." These provisions of the law are in accordance with constitutions of a number of the western states; for instance, Colorado, California, North Dakota, Washington, Wyoming, and Idaho.[1]

In these newer states the constitutional provisions and laws embodying the same principles in other states have been upheld by the courts. Unfortunately in Wisconsin, before the value of the energy of falling water was appreciated, the courts had made various decisions which limited the right of the state in the waters of navigable streams to that of navigation, fishing, etc.; but general legislative enactment has never been made in which the right to develop the energy of the falling water has been declared to appertain to the riparian; and no general decision of the court had been made upon this matter at the time the above law was passed. The legislature in granting franchises for the development of water power, had, with the exception of a few of the earliest ones, included the provision that they are subject to amendment or repeal; and also that state constitution contains the provision that all general or special acts regarding corporations may be altered or repealed by the legislature at any time after their passage. However, for many years the energy of falling water had been utilized by many riparian owners under the special acts of the legislature authorizing the building of dams for the improvement of navigation.

---

[1] Conservation of Natural Resources in the United States, C. R. Van Hise, pp. 153–154.

The supreme court of the state in January, 1912, declared the act, making a franchise charge upon the use of water power, unconstitutional. The opinion of Justice Timlin, accompanying this decision, contained the dictum that "the right of the riparian owner to use the water of the river on his own land within his boundary determined by ordinary high water mark, for the purpose of creating power or, as the act in question puts it, 'developing energy,' returning the water again to the stream, is unquestionably a private right appurtenant to the riparian land."

This dictum appears to affect not only water powers, franchises for which have already been granted and development made, but it affects the half a million or more of undeveloped water power in the state.

Why the decision should be extended to the undeveloped water power nowhere appears in the opinion rendered. The right of the riparian to the developed water powers is recognized upon the basis that the legislature granted the charter "in consideration that the grantee would make the improvement in aid of navigation; the latter accepted the offer and invested thousands of dollars in making the improvement" . . . "By contract with the state, therefore, the riparian owner bought and paid for this valuable property right so far as the state had power to grant it. He had also acquired by purchase the riparian right hereinafter referred to."

Admitting the full force of these statements, the argument does not apply to undeveloped water powers.

If the dictum of the court be accepted as law, the owners of the riparian rights upon meandered streams have come into possession of a property of enormous value, without cost and thru judicial decision. To illustrate: If in the future there are developed 500,000 additional horse power and the value of such horse power for creating energy should prove to be $5 per annum, this on the basis of five per cent would represent a capitalization of $50,000,000. The situation appears to be that thru the decision of the courts more than one half of the water power of the state has been granted to the riparian without compensation.

If the opinion of Judge Timlin stands, apparently the best that can be done in Wisconsin regarding the water powers is to amend the constitution so that the state may acquire and operate them and pass laws giving to the state municipalities the right to acquire water powers thru condemnation and to operate them as public utilities. A bill to this end was introduced in the special session of the legislature in 1912, but it failed of passage; therefore the entire subject of the general regulation of water powers has gone over to the legislature of 1913.

The recommendation of the conservation commission that hereafter franchises for water powers be granted under a general act and that the administration of this act be placed under some commission seems to be the accepted policy of the state. This is however small solace for the loss of the energy of the falling waters of the streams of the state which should belong to the people. It appears to me personally that the conservation commission should make another effort to have a bill passed which at least will save the energy of the falling water of those powers in which franchises have not been granted. If this can be accomplished it will still save for the people about one half of the water power resources of the state.

FORESTS

Creation of Forest Reserve. Twenty-five years ago Wisconsin was one of the greatest and wealthiest forest regions in the United States, and the twenty-seven counties which comprised the northern portion were practically an unbroken forest extending from Michigan to Minnesota. Even as late as 1900, Wisconsin ranked first among the states in the production of lumber, but by 1910 it had dropped to eighth place.

The axe, followed by terrific forest fires, has depleted the great forest wealth of the state; and when it is almost too late the state is waking up to appreciate something of the value of this wonderful, natural resource, which has been dissipated so recklessly.

As early as 1867 a law was passed providing for the appointment of three commissioners to investigate and report upon the injurious effects of clearing the land of forests and the duty of the state in regard to the matter. An exhaustive and very valuable report was published by the three commissioners, but no results were accomplished. In 1897 another law was passed providing for the appointment of a forestry commission of three members by the governor, who were to draw up a plan for the protection and utilization of the forest resources of the state, for the organization of a forestry department, and for the creation of a forest reserve. The commissioners' report, including a draft of a bill which they recommended for passage, was published in 1898, but no legislation resulted until 1903 when a forest reserve of about 40,000 acres was created. But the first effective forestry legislation was not accomplished until 1905. Under the law of 1905 a non-political state board of forestry was created, and it was provided in the act that the state forester, to be appointed by the board, must be a technically trained forester and certified as such by the secretary of the United States Department of Agriculture. The most important provision of this law was that all state lands in the northern, or timbered, portion of the state were set aside for forestry purposes, and that the agricultural and scattered lands could be sold by the board, the proceeds to constitute a "forest reserve fund" to be used in purchasing lands suitable for enlarging the forest reserve area. The law of 1905 included in the state forest all state lands in the northern portion of the state. This immediately increased the area of the reserve from 40,000 acres to over 300,000 acres. State appropriations for the extension of the forests were made in 1911. Through the purchases of privately owned lands over 100,000 acres, at an average cost of $3.00 per acre, have been acquired, so that the reserve today totals some 425,000 acres, and contracts for purchases when executed will increase the total to about 475,000 acres.

It thus appears that the conservation movement in the state of Wisconsin, so far as the forests are concerned, began before the White House Conference and the appointment of the state conservation commission. A number of recommendations of the commission regarding forestry were however enacted into law, and therefore the work of the commission may be said to have accelerated the movement for state forests. Among the recommendations adopted were a direct state appropriation for additions to the forest reserve, an increase in the appropriation for the administration of the reserve, and making the land in the Menominee Reservation a part of the reserve. Recommendations were also made that the state constitution be amended so as to prevent the taxation of timber land, by a method which would tend to preserve the forests instead of destroy them. A system of compulsory patrol and the burning of slashings by the state in private forests in the forest belt were recommended. Realizing that no general regulations are applicable to the burning of slashings or to patrol, it was advocated that the formulation of the regulations upon these matters and their execution be under the state board of forestry.

Character of Forest Reserve. It is difficult to draw a clear picture of the Wisconsin forest reserve since some portions have very heavy stands of virgin timber, others promising young growth, while large areas are either restocking naturally or have been so badly burned that they must be replanted. The finest bodies of timber which the state owns within the forest reserve area are on the 16,378 acres within the Menominee Indian Reservation, and on the 35,427 acres which the state owns in Forest county. The timber upon the Menominee Reservation is white pine, which grows in mixture with magnificent hardwoods, principally basswood, birch and maple. On the Forest county lands the timber on the ridges is white and Norway pine in mixture, with hemlock, basswood, birch, maple and elm. On the lower ground hemlock predominates and in the swamps there is good cedar and spruce.

Within the Lac du Flambeau Indian Reservation, which is in the heart of the forest reserve, the state owns 20,666 acres, and in the northern portion of the reservation there are some splendid stands of virgin white pine, while on the poorer sandy soils the timber is largely Norway pine.

The balance of the state forest reserve lands are located in a number of counties. The lands which are suitable for agriculture, or so widely scattered that they cannot be used for forest reserve purposes, will be sold and the proceeds used to purchase other lands to block up the permanent forest reserves.

It is felt that satisfactory progress has been made in increasing the forest reserve from 40,000 acres to 425,000 acres in seven years, but Wisconsin has only made a good start for the state should have a reserve of about 1,500,000 acres in order to meet the future needs.

The forest reserve lands in Price and Iron counties, which comprise some 57,000 acres, are typical hemlock and hardwood ridges, with some cedar, spruce, and balsam in the swamps. Some fifteen to twenty years ago the large white pine was cut on these lands, but a young growth of pine timber is coming up which only needs protection from fire to become a fine forest.

The state owns some 123,000 acres in Vilas county and 57,000 acres in Oneida county. The lands in Vilas and those in the Northern part of Oneida county, will constitute the backbone of the permanent forest reserves, as they lie at the headwaters of the Wisconsin and Chippewa Rivers, and also in the heart of the beautiful lake region. The lands in northern Oneida county are largely covered with hemlock and hardwood on the ridges, and on the level, sandy plains, from which the virgin pine was cut many years ago, the young pine growth is in most sections most promising and very little planting will be necessary. On the forest reserve lands in the eastern and northern portions of Vilas county, there is upon the whole a fairly heavy stand of hemlock and hardwoods, with scattering white and Norway pine. In the central portion of the county the virgin stand of pine was so dense that the cutting was very heavy, and the forest fires which followed the slashings of the lumberman were so severe that all the remaining timber was destroyed. However, there was a large amount of pine seed buried in the thick humus and where the fires have not burned too deeply the young white and Norway pine seedlings are beginning to appear.

Just how much of the burned over land must be replanted, it is impossible to tell, but it is probable that a very considerable percentage will be restocked naturally.

State Forest Policy. What specific objects has Wisconsin in view in creating her forest reserve? The state is building up her reserve in some of the most northerly counties, viz.: Forest, Vilas, Oneida, Iron and Price, and within this area there is not only a wonderful lake region of over 1,200 lakes, but also the headwaters of four of the greatest rivers in the state, viz.: the Wisconsin, Chippewa, Menominee, and Wolf.

The state lands set aside for the reserve, as also the lands purchased, are not suitable for agriculture, being either too sandy, rocky, or swampy, but these lands have grown some of the finest pine timber in the state, and all the young timber needs is protection from fire. The state forest policy then is looking to the accomplishment of the following points, viz.:

(1) Extensive forests should be maintained upon the headwaters of the important rivers. This together with the use of many lakes as storage reservoirs will tend to make the flow of these rivers regular, thus preserving and even improving many waterpowers which will become increasingly valuable, especially since Wisconsin has no deposits of coal.

Wisconsin has adopted the policy of allowing river development companies, under careful state supervision, to use many of the lakes at the headwaters of the Wisconsin and Chippewa rivers as reservoirs, so as to hold and store up the excess or flood waters, which may be drawn upon at times of low water. No new storage dam can be built without the consent of the state board of forestry and the board also controls the level to which the water may be raised or lowered, so that the beauty and attractiveness of the lakes for summer camps and cottages will always be carefully protected. With a large forest reserve surrounding these lakes, thus preventing the deep snows from melting too rapidly, and the lakes as storage reservoirs holding back the spring freshets, the stream flow of the Wisconsin and Chippewa rivers can be systematically regulated, and thus the waterpowers will gain enormously from a constant and even flow. Wisconsin has gone much farther than the other states in developing a definite policy looking to the full development of storage reservoirs and the forest reserve will always protect the reservoirs from silting up.

(2) In 1910 a study of the wood-using industries of Wisconsin was made in coöperation with the United States Forest Service and it was found that more than 930 million board feet of lumber valued at $20,000,000 is annually utilized in the wood-using

industries, and that already almost fifty percent of this lumber is purchased outside of the state. This means that in time the state will lose its wood-using industries unless the rapid destruction of the forests is checked. A state forest reserve of 1,500,000 acres can aid very materially in supplying this raw material.

If Wisconsin had been as wise as Canada and retained its timbered lands instead of selling them, the forester would have a going concern and the timber would be his stock, which he would sell as it became mature and thus be able to show a revenue at once. But Wisconsin chose in the past to sell its timber lands to anyone and everyone at a fraction of what their present value would be. Therefore the state must buy back the timberlands that it sold, and it will be many years before there will be much merchantable timber to sell from the forest reserve. The bright side, however, is that much of the timber that was left is now, with increasing demands, becoming valuable.

Taking into consideration the acreage of land within the forest reserve that contains virgin timber and that which is fairly well timbered, also the areas that contain only young growth and those that must be planted, it is not probable that in twenty-five years the state will receive a net revenue of over $1.00 per acre, but at the end of fifty years this should increase to at least $2.00 per acre. The probable revenue from the firewood and all other forest products is included in this estimate; also the revenue from leasing camp and cottage sites, which will be very considerable. If then the state acquires a forest reserve of 1,500,000 acres, it should be able to count on a net annual revenue of $1,500,000 after twenty-five years, and of $3,000,000 after fifty years.

(3) Preserving the forests in the beautiful lake region of northern Wisconsin will greatly enhance its present attractiveness as a resort region, not only for the citizens of the state, but of the entire Mississippi valley as well. The value of such a resort region is not generally understood, even from the dollar view point; but the report of the bureau of labor of New Hampshire for 1905 shows that the resort business yielded in that year over $10,000,000, and the report of the forest, fish and game commission of New York for the same year states that it was over $7,000,000.

The state board of forestry has adopted the policy of leasing camp and cottage sites upon the shores of the beautiful lakes within the forest reserve. Owning several thousand acres of land upon the shores of some of the most attractive lakes in Oneida and Vilas counties, the state is easily able to meet upon reasonable terms all present demands for sites of various kinds.

As Ex-President Roosevelt has so well pointed out, the National forests as well as the forest reserves maintained by the various states are intended for the fullest and best use consistent with their protection, and one of the most natural uses to which a portion of the reserves should be put is as fish and game preserves; and this will greatly enhance their value for resort purposes.

Forest Planting. In 1911 nearly 200,000 seedlings were planted on lands within the forest reserve which were not restocking naturally, and the state now has over 1,400,000 seedlings, in one large nursery, which will be utilized in planting denuded lands. It has been discovered, however, that a large percentage of the cut-over lands in northern Wisconsin will restock naturally, provided that forest fires have not burned over the land so frequently as to destroy all the seeds in the soil. Therefore it is not expected that many large tracts will have to be planted.

It is the intention of the state board of forestry to sell plants at cost to individuals and corporations who may wish to reforest their denuded non-agricultural land.

Fire Prevention on the Forest Reserve. The state board of forestry has a force of rangers and patrolmen whose chief duty it is to see that any forest fires which start upon the forest reserve are promptly extinguished. When active patrol work is not necessary, these men take charge of the crews who are engaged in cutting roads, trails, and fire lines, and in constructing telephone lines or destroying dangerous slashings.

The object of the roads, trails, and fire lines is to divide the forest reserve into a large number of blocks or compartments so that if a forest fire starts it can be held to the block of land in which it originates. By means of the lookout towers and telephones the rangers can readily locate forest fires and then summon the necessary help without any loss of time. In order to patrol their districts as rapidly as possible most of the rangers either have saddle horses or railway velocipedes.

Forestry by Private Owners

To the present time in Wisconsin very little real forestry management has been practiced by lumber companies, large timberland owners, or private individuals. This has been largely due to the danger of timberlands being destroyed by forest fires, and also the annual taxing of growing timber which has encouraged forest destruction instead of forest conservation.

Many of the large wood-using industries of the state, especially the paper and pulp mills, should own large tracts of timber and operate under a systematic plan of forest management; but many are held back from doing this on account of the fear of fires and taxes. The first can and will be overcome through education of the people to the fearful and needless losses from forest fires, together with well organized forest fire patrols; and the second obstacle will be removed when the state appreciates that the present system of annually taxing growing timber is archaic and that it directly encourages and even forces forest destruction.

Parks

Closely connected with forests are parks. The importance of parks and playgrounds for the health and happiness of the people has not been generally appreciated in this country. In consequence of this, many large cities have an entirely inadequate park system and the majority of states have scarcely begun to realize the importance of a number of parks conveniently situated to be the common property of the people.

In Wisconsin in 1907 a park board was created and appropriations were then and later made for acquiring state parks. Two of the most picturesque areas in the state have been secured. One of these is in Door county on the peninsula extending east into Lake Michigan, containing eight miles of shore line. The second park is in the uniquely beautiful Devil's Lake area. Prior to 1907, by coöperation with the state of Minnesota, the Dalles of the St. Croix River had been acquired as an inter-state park. In addition for provisions for state parks, laws had been enacted giving to cities very large authority in acquiring parks. Already Milwaukee and Madison have taken advantage of these laws and the same is true to a less extent of other cities. In the future this movement, which will result in numerous parks of moderate size, both state and municipal, will be recognized as one of far sighted wisdom.

Soils

The land is the basal resource of the nation, is indeed more important than all other resources. From the land come our food and clothing. Food and clothing we must have; all of our other needs are subordinate to these. While the preservation of the fertility of the soil is the most fundamental of the problems of conservation, so also it is the most difficult. Many of the owners of the soil have very imperfect knowledge and little sense of responsibility regarding its preservation. In the rather sparsely settled United States, where until recently rich, virgin land has been free, there has been wastefulness in the exploitation of the land such as perhaps has existed nowhere else in the world.

Realizing this situation, from the first the Wisconsin conservation commission has directed its attention to the conservation of the soil. In the state of Wisconsin there are more than 175,000 farms. The problem is to get a vast number of farmers so to handle their soil as to enrich instead of diminish its fertility. While Wisconsin is one of the relatively new states and the larger portion of its lands has not been cultivated on an average for as much as fifty years, already there is serious depletion in the fertility of large areas. The efforts to secure the conservation of the soil of Wisconsin have proceeded along three lines: (1) education, (2) investigation, and (3) legislation.

(1) The most comprehensive and satisfactory way to secure the conservation of the soil is to educate the farmers regarding scientific methods in order that they may so handle their lands that they increase in fertility rather than decrease. This problem of education, while very large, is hopeful because of the fact that the practices advocated will in the long run work to the

advantage of the farmers as well as to the advantage of the state and nation. In a brief paper it will be impossible more than to mention some of the lines of effort which have been directed to the education of the farmers of Wisconsin.

At the University of Wisconsin, in addition to a four year college course in agriculture, there are a two year course of a more practical character, and still shorter general courses, dairy courses, courses for farmers, etc. Further, the college has undertaken agricultural extension upon an elaborate scale, with the idea of carrying out to the farmers through demonstration and illustration improved agricultural practices. In a considerable number of counties there are county schools of agriculture which are designed especially to give training for the farmer. By the action of the legislature of 1911, high schools which contain agricultural courses are granted special state aid. This was recommended both by the conservation commission and the commission on industrial education. Provision is made for agricultural instruction in the county training schools, twenty-six in number, the duty of which is to prepare teachers for the rural schools. Thus the entire system of education from the University to the rural schools is designed to tend to conservation of the soil.

(2) Investigations relating to the conservation of the soil are being pursued along many lines.

The first report of the commission recommended a soil survey. An appropriation was made for this purpose by the legislature of 1909. This work in coöperation with the United States survey is being actively pushed. To the present time a detailed survey has been finished for more than 5,500 square miles. A reconnaissance survey of the northern part of the state has been made for an area of 4,500 square miles. One of the purposes of this reconnaissance survey is to determine lands which are better adapted for agriculture than for forestry.

Some of the questions under investigation by the college of agriculture, are soil erosion, the preservation of the essential elements of the soil, the eradication of weeds, and agricultural economics.

For parts of the state the depletion of the soil is due largely to erosion, in other parts mainly to depletion of essential elements; altho thruout the state almost everywhere both are important factors. In regard to the loss of soil thru erosion the state is being studied in relation to its topography and the character of the soil, in order to formulate methods of cultivation adapted to the situation. However, for much of the state the question of depletion of essential elements is no less important than erosion, and no where else has this problem been more seriously attacked. In this brief paper it is quite impossible to take up in detail the methods which are being worked out for the prevention of erosion and the reduction of loss of essential elements. The general principles of these matters are well known, but in each state these principles must be adapted to the particular conditions.

A very important factor in the depletion of the soil is noxious weeds. For many counties in the eastern part of the state large areas are badly infested by such weeds, among which Canada thistle and quack grass are the worst. Not only is there a considerable portion of the state thus weed infested, but the area is extending. These weeds make heavy drafts upon the fertility of the soil, and where present greatly decrease the amount of the crop. Already investigation has shown that quack grass and Canada thistle can be eradicated by at least two methods. Having found successful economic methods for eradicating these weeds, a campaign of education is being carried on among the farmers to produce their destruction.

The economics of agriculture have scarcely been considered by farmers in this county, altho cost accounting has been introduced into business for many years. In most cases, when a farmer sells his crop he does not take into account the question of whether his soil has been enriched or depleted as a result of the operation. Professor H. C. Taylor says:

"Types of farming have been studied from the standpoint of their influence upon the future usefulness of the soil. Two leading types of farms in Wisconsin are grain and dairy farms. Commercial fertilizers are rarely used on grain farms in this state; hence grain farming means exploitation, while dairy farming stands for soil maintenance. In the early history of Wisconsin, wheat farming dominated. In a few decades, soil exhaustion and other causes led to the abandonment of the selling of grain in favor of the selling of butter and cheese. The readjustment has been in progress for thirty years, but is not yet complete. The greater profits of dairying have led the more intelligent farmers to make the change, but many are so bound by habits of thought and action that only the stern hand of economic necessity will drive them to make a change in their methods."

(3) The third stage, that of specific legislation for the preservation of the soil, has no more than begun. Laws have been placed upon the statute books prohibiting the importation into the state of impure seeds, and especially those infested with deleterious weeds. The Director of the Agricultural Experiment Station has been given authority to inspect nursery stocks, with reference to the prevention of the importation of infective plants. Laws have been passed which make it the duty of local officials to extirpate noxious weeds; but as yet these laws are largely a dead letter and will be until the legislation is so modified as to place the execution of the law in the charge of state officials who have as their special duty the execution of these laws. This the conservation commission has recommended, and an act to this end will be vigorously pushed at the next session of the legislature.

While great improvements have been made in the agricultural practices of the state looking toward the lessening of erosion and depletion of the valuable elements, a balance sheet shows that to the present time Wisconsin has not nearly reached a condition in which upon the average the land of the state is richer at the end of a given year rather than poorer; and this notwithstanding the fact that the state is one of the greatest in its dairy interests. Thus for phosphoric oxide, the most crucial element of the soil, it is estimated that the annual loss to the state is 15,000,000 pounds. The largest loss is due to the waste of manure by washing the same into the streams. Another large loss is through sewage and another part is due to leaching of exhaustive crops, such as tobacco.

It is clear that the campaign of education and investigation in Wisconsin with supplementary legislation must go on until the balance sheet shows increased fertility upon the average rather than decreased fertility; for only thus will it be possible one hundred years hence for the state to produce food for its large population.

The situation above described illustrates how great is the problem of education, investigation, and legislation, which confronts the states of the Union, in the vast majority of which, if not in all, the situation is less advantageous than in Wisconsin.

Minerals

Progress has been made in the conservation of mineral resources of the State of Wisconsin only to the extent of surveys and investigation. The first step in these matters is to find out the facts. In the southwestern part of the state the losses in the mining and extraction of lead and zinc are very great. It is estimated that only a little more than one half of the zinc in the ground becomes spelter; thus the loss is nearly fifty percent. Some thirteen and one half per cent of this loss is in mining; the remainder is mainly in milling and smelting. The large loss in mining is due to the very high royalty; ten per cent of the concentrated product, which is paid to the fee holder. If this rate were decreased for lower grade ores, they could be profitably extracted in connection with the richer ores, whereas they are now left in the ground. The conservation of the metallic ores is also related to the system of taxation.

The question of remedying the great losses in zinc beginning in the southwestern part of the state and a system of taxation for zinc and for iron ore are subjects which are under investigation by the state conservation commission, with the hope of being able to make recommendations to the legislature at their next session.

General Statements

In the second report of the state conservation commission the desirability of a general law regarding conservation was pointed out and it was shown that if such a law were possible it would be supported by the highest courts, state and national. A bill to this end was therefore prepared and was by the legislature of 1911 enacted into law.

The essential parts of the law are as follows:—

"1. It is hereby made unlawful for any person, firm or corporation, unreasonably to waste or maliciously to injure, destroy, or impair any natural resource within this state.

"2. It is the purpose of this act to promote and secure the conservation of the natural resources within the state in the interests of the public welfare."

This is probably the only comprehensive law yet enacted by any state which includes the fundamental principles which should obtain in regard to conservation. At the outset this law may not produce much effect, but it is believed that it will have an increasing potentiality as the years go by. It can be invoked at once to prevent the wasting of artesian water either carelessly or maliciously. As soon as it can be shown to be practicable and economical to save the branches and tree tops in the cutting of forests, the law may be invoked to compel such utilization. If a farmer wantonly allows gullies to form in his farm, and thus permit unnecessarily rapid erosion either to the injury of his own land or to that of his neighbors, this law may be invoked to compel the delinquent farmer to take the necessary steps to stop the destruction of the soil, the most important resource of the state.

It has been found necessary to have special officers to enforce the pure food laws. In order that this general conservation law shall produce its full effect, it will be necessary to have special administrative officials whose duty it will be to see to its enforcement. As soon as public sentiment has sufficiently developed so that such offices are created this law will have a controlling influence in the conservation of the resources of the state.

Under the broad charter of this law it is the plan of the state conservation commission to move forward carefully, but as rapidly as public sentiment will support the commission. The commission plans to present at the next session of the legislature recommendations adopted to the new situation in the water powers, and recommendations regarding the extension of forests, the drainage of swamp lands, the reduction of the losses of lead and zinc, the taxation of ores and mineral rights, the conservation of the soil, and the destruction of noxious weeds.

The conservation commission fully appreciates that with reference to the future of the people of the state the conservation of its natural resources is of greater importance than any and all other questions before the people. The recommendations of the commissioners have thus far received a response from the legislature quite beyond their expectation. Therefore they look forward confidently to a continuation of the progress of the conservation movement in Wisconsin until the time comes when it can be said that the natural resources of the state are transmitted to the succeeding generation unimpaired. This should be the aim and the ideal of each state conservation commission. When it is accomplished the foundation of the future prosperity of the nation will be assured.

GENERAL INDEX
TO THE TWENTY-FOUR VOLUMES OF ORIGINAL COMMUNICATIONS

Volume	Section	
1	I.	Analytical Chemistry.
2	II	Inorganic Chemistry.
3	IIIa	Metallurgy and Mining.
4	IIIb	Explosives.
5	IIIc	Silicate Industries.
6	IV	Organic Chemistry.
7	IVa	Coal Tar Colors and Dyestuffs.
8	Va	Industry and Chemistry of Sugar.
9	Vb	India Rubber and other Plastics.
10	Vc	Fuels and Asphalt.
11	Vd	Fats, Fatty Oils and Soaps.
12	Ve	Paints, Drying Oils and Varnishes.
13	VIa	Starch, Cellulose and Paper.
14	VIb	Fermentation.
15	VII	Agricultural Chemistry.
16	VIIIa	Hygiene.
17	VIIIb	Pharmaceutical Chemistry.
18	VIIIc	Bromatology.
19	VIIId	Biochemistry including Pharmacology.
20	IX	Photochemistry.
21	Xa	Electrochemistry.
22	Xb	Physical Chemistry.
23	XIa	Law and Legislation Affecting Chemical Industry.
24	XIb	Political Economy and Conservation of Natural Resources.